

INSTITUTE OF METALS
DIVISION

1940

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AND METALLURGICAL ENGINEERS**

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INSTITUTE OF METALS DIVISION
1940

PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD AT
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Notice

This volume is the fourteenth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Chicago Meeting, Oct. 23-25, 1939, and the New York Meeting, Feb. 12-15, 1940. The complete list of publications and proceedings, including the present volume, is as follows:

- 1908-1911 *Transactions* of the American Brass Founders' Association: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.
- 1912-1916 *Transactions* of the American Institute of Metals, Vols. 6-10.
- 1917-1918 *Journal* of the American Institute of Metals, Vols. 11-12.
- 1919-1926 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.
- 1927-1928 *PROCEEDINGS* of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, two volumes, of which the later is now designated Vol. 78 of the A. I. M. E. *TRANSACTIONS*.
- 1929-1940 *TRANSACTIONS* of the American Institute of Mining and Metallurgical Engineers, Volumes 83, 89, 93, 99, 104, 111, 117, 122, 124, 128, 133 and 137, Institute of Metals Division.

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FOREWORD

This volume of the TRANSACTIONS—the fourteenth of the Institute of Metals series—contains 32 papers dealing with metallurgical phenomena of current and permanent interest, which represent an enormous amount of painstaking work on the part of the authors.

Five papers deal with the constitution of important systems. Three are primarily concerned with the strength properties of alloys but additional information dealing with mechanical properties is presented, incidentally, in several other papers concerned primarily with other problems. Seven papers relate to deformation and recrystallization, one to aspects of oxidation that are important in the annealing of copper alloys, while one deals with corrosion phenomena under static stress.

The breadth of subjects covered and the quality of the papers is apparent. Much credit should be given to the chairman, Cyril Stanley Smith, to the vice-chairman, E. E. Schumacher, and to the members of the Papers and Programs Committee for their untiring work in organizing meetings and in editing materials for this volume.

The Annual Lecture, by E. H. Dix, Jr., Chief Metallurgist of the Research Laboratories of the Aluminum Company of America, on "Acceleration of the Rate of Corrosion by High Constant Stresses," is outstanding in this series of Annual Lectures. The lecturer clarified the relations between stress and the electrochemical aspects of corrosion that are responsible for "stress cracking" and thus removed much of the mystery which has veiled this phenomenon to which both ferrous and nonferrous alloys may succumb.

The work of the Membership Committee is extremely important and the effort that has been given to it by L. R. Van Wert, the chairman, and by the members of his committee is greatly appreciated.

As Chairman of the Division, I want to thank the members at large, the officers, the chairmen and members of the various committees for their efforts in carrying forward the work of the Institute of Metals Division.

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ANNUAL AWARD CERTIFICATE OF THE INSTITUTE OF
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In 1933, the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers established its annual award of an engraved certificate to the author or authors of the paper that in the opinion of the award committee represents the most notable contribution to metallurgical science among the papers that have been accepted by the Division for presentation at one of its meetings and have been published by the Institute within the three years preceding the date of award. The award is made by the Division each February. There are no restrictions with respect to nationality, age or occupation of the author or authors.

Awards have been made as follows:

- 1934 Robert F. Mehl and Charles S. Barrett: Studies upon the Widmānstatten Structure, I—Introduction. The Aluminum-silver System and the Copper-silicon System. TRANSACTIONS (1931) **93**, 78–110.
- 1935 E. A. Anderson, M. L. Fuller, R. L. Wilcox and J. L. Rodda: The High-zinc Region of the Copper-zinc Phase Equilibrium Diagram. TRANSACTIONS (1934) **111**, 264–292.
- 1936 Cyril S. Smith and W. Earl Lindlie: A Micrographic Study of the Decomposition of the Beta Phase in the Copper-aluminum System. TRANSACTIONS (1933) **104**, 69–105.
- 1937 Arthur Phillips and R. M. Brick: Effect of Quenching Strains on Lattice Parameter and Hardness Values of High-purity Aluminum-copper Alloys. TRANSACTIONS (1934) **111**, 94–112.
- 1938 William L. Fink and Dana W. Smith: Age-hardening of Aluminum Alloys, I—Aluminum-copper Alloy. TRANSACTIONS (1936) **122**, 284–293.
- 1939 Frederick N. Rhines and Robert F. Mehl: Rates of Diffusion in the Alpha Solid Solutions of Copper. TRANSACTIONS (1938) **128**, 185–221.
- 1940 Alden B. Greninger: Martensite Transformation in Beta Copper-aluminum Alloys. TRANSACTIONS (1939) **133**, 204–221.

THE INSTITUTE OF METALS LECTURE

AN annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. In 1934 the Division established the custom of presenting a certificate to each lecturer.

A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.
- 1933 Present-day Problems in Theoretical Metallurgy. By Georg Masing.
- 1934 Ferromagnetism in Metallic Crystals. By L. W. McKeehan.
- 1935 Gases in Metals. By C. A. Edwards.
- 1936 Diffusion in Solid Metals. By Robert F. Mehl.
- 1937 Refractories. By R. S. Hutton.
- 1938 The Nature of Metals as Shown by Their Properties under Pressure. By P. W. Bridgman.
- 1939 The Creep of Metals. By D. Hanson.
- 1940 Acceleration of Rate of Corrosion by High Constant Stresses. By Edgar H. Dix, Jr.



EDGAR H. DIX, JR.

Parry, Pgh.

Institute of Metals Division Lecturer, 1940

Acceleration of the Rate of Corrosion by High Constant Stresses

BY E. H. DIX, JR.,* MEMBER A.I.M.E.

(Institute of Metals Division Lecture†)

IN selecting the subject, "Acceleration of the Rate of Corrosion by High Constant Stresses," for the 1940 Institute of Metals Division Lecture, I have been influenced by its highly theoretical and speculative nature as well as by the great practical importance of the correct interpretation and appraisal of the engineering significance of the phenomenon. I lay no claim to originality in talking on this topic, since it has been the subject of discussion for over a quarter of a century. However, as our technical thinking advances, old phenomena take on new and more significant aspects. In our studies at the Aluminum Research Laboratories, we have encountered many perplexing and seemingly contradictory results and have been fascinated by the problem of dovetailing all of the many pieces of information to make a complete picture. I hope that in the brief period of this lecture I may share with you some of the enjoyment we have had in attempting to meet this challenge to metallurgical science.

The emphasis generally has been placed on the spontaneous failure by cracking of a metal under the combined action of high stress and corrosion, hence the present-day use of the terms "stress corrosion" or "stress corrosion cracking." The older term "season cracking," applied more specifically to copper-base alloys, includes, by inference, the element of time. For the purpose of the discussion today I will use "stress corrosion" to cover broadly the effect of stress in accelerating the rate of corrosion of metals. To stay within the limits of allotted time the discussion will cover the effect of high static stresses rather than repeated or dynamic stresses, which would take us into the related field of corrosion-fatigue.

The subject is particularly appropriate for an Institute of Metals Division Lecture because much the same phenomenon has been observed in almost all metal systems. Thus, in addition to the season cracking of brass may also be mentioned the "caustic embrittlement" of steel boiler

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† Presented at the New York Meeting, February 1940. Nineteenth Annual Lecture. Manuscript received at the office of the Institute March 12, 1940. Issued as T.P. 1204 in METALS TECHNOLOGY, June 1940.

plate, the "embrittlement" of lead cable sheath and the "spontaneous cracking" of the old, impure, zinc-base die-casting alloys. Certain aluminum alloys and some types of stainless steel are also known to be susceptible to stress corrosion.

The principal factors in stress corrosion vary greatly in their relative influence and may interact, one accelerating the action of another. These factors are stress, corrosive environment, time and the internal structure of the alloy. The internal structure is dependent upon the composition, method of fabrication ("as cast," hot-worked or cold-worked), thermal treatments and often the extent of natural aging.

Aging, as I expect to show during the course of this discussion, plays a very important role in determining whether or not a metal will be susceptible to acceleration of corrosion by stress. It is particularly appropriate, then, that stress corrosion be discussed but a few months subsequent to the comprehensive symposium on precipitation-hardening at the last National Metals Congress.

The literature on the subject of stress corrosion is voluminous and it will not be possible to cover, even superficially, the many important articles on this subject. Rather, it shall be my purpose to treat the subject in a speculative manner in the hope that the new experimental evidence presented and the theory of the mechanism of stress corrosion suggested will lead to a better understanding of the phenomenon among metallurgists interested in the different metal systems and will aid in a more intelligent engineering appreciation of its practical significance.

About a quarter of a century ago, E. Heyn, in the May lecture of the British Institute of Metals, chose for his subject Internal Strain in Cold Wrought Metals, and Some Troubles Caused Thereby.¹ While that lecture was devoted primarily to a consideration of the mechanical aspect of the effect of stress, the influence of surface damage produced by localized corrosion was recognized. In 1918, the significance of corrosion in the season cracking of brass was well recognized in a discussion on this subject² contributed to by such well-known metallurgists as William Campbell, W. H. Bassett, W. R. Webster, P. D. Merica, W. B. Price, H. S. Rawdon and C. H. Mathewson. Yet, in 1919, Rosenhain and Archbutt,³ in attempting to explain the mechanism of the failure of some high-zinc aluminum-base alloys, ignored the significance of the role of corrosion and suggested that viscous flow of the amorphous material at smooth, regularly formed grain boundaries was responsible for the cracking. Rosenhain also defended this theory in 1922 in discussing the failure of metals under internal and prolonged stress,⁴ although apparently without convincing C. H. Desch, L. Archbutt, W. H. Hatfield, D. Hanson, O. W. Ellis and others who also participated in the discussion. The

¹ References are at the end of the paper.

excellent correlated abstract on the embrittlement of boiler steel, by Partridge and Schroeder⁵ also should be mentioned as illustrating the mass of conflicting literature available on only one phase of this wide subject. The author, in preparing this lecture, has more than once regretted his temerity in selecting such a broad and frequently discussed subject. Many of the ideas that will be expressed today have been advanced by others at various times in the past. However, it is hoped to be able to present a fresh aspect and a somewhat different emphasis, as indicated by the title, "Acceleration of the Rate of Corrosion by High Constant Stresses."

As so often occurs, practical solution has preceded acceptable scientific explanation. The season cracking of brass has been largely eliminated by low-temperature annealing to minimize the internal stress. Zinc-base die castings have been greatly improved by the use of very high-purity zinc and the addition of certain corrective elements. Caustic embrittlement of boilers has been practically overcome by the proper selection of steel and suitable treatment of boiler waters. More suitable aluminum alloys have replaced the high-zinc compositions, and the stress cracking of stainless steel is being avoided by corrective additions, proper thermal treatment and pilot tests, such as are described by Hoyt and Scheil,⁶ to determine the type of steel best suited for a new application.

Since the time of Rosenhain's stress-cracking experiments with the high-zinc, aluminum-base alloys, the commercial aluminum alloys have been peculiarly free from service failures attributable to stress corrosion. However, within recent years the industrial utilization abroad of a new group of strain-hardened high-magnesium, aluminum-base alloys has again drawn attention to this phenomenon and the recent literature,⁷⁻¹³ particularly in Germany, is replete with articles discussing the stress corrosion of these alloys and methods of prevention that are being studied.

In our own experience, about ten years ago, a very spectacular example of stress corrosion closely resembling the season cracking of brass was encountered. A pan drawn from cold-reduced sheet, which had not been subsequently annealed, of an aluminum-magnesium alloy containing 10 per cent Mg, was found to be in the condition shown in Fig. 1 after a few months during which New Kensington tap water was stored in it. This experience, fortunately occurring in the early stages of the investigation, focused attention on the possibility of this type of failure in new and untried alloys and resulted in a rather extensive research on this phenomenon by the writer and his co-workers. The wisdom of this procedure became evident in comparison with the procedure abroad, where certain of these alloys achieved considerable engineering use before this characteristic was discovered.

In any modern industrial laboratory, research is a coöperative effort, in which a group of experts bring their specific knowledge to bear on the

problem in hand and the result, achieved through this effective manner of operation, is truly the result of teamwork in which one person, such as your lecturer, has only a small part. Were I to attempt to give credit to all the individuals who have had a part in the researches contributing toward this lecture I would have to name a large number of the personnel of the Aluminum Research Laboratories. I shall mention but a few in the course of this discussion but I here wish to acknowledge my indebtedness and appreciation to the Director and Assistant Directors of the Aluminum Research Laboratories and to the management of the Aluminum Company of America for the far-sighted and broad-minded policies

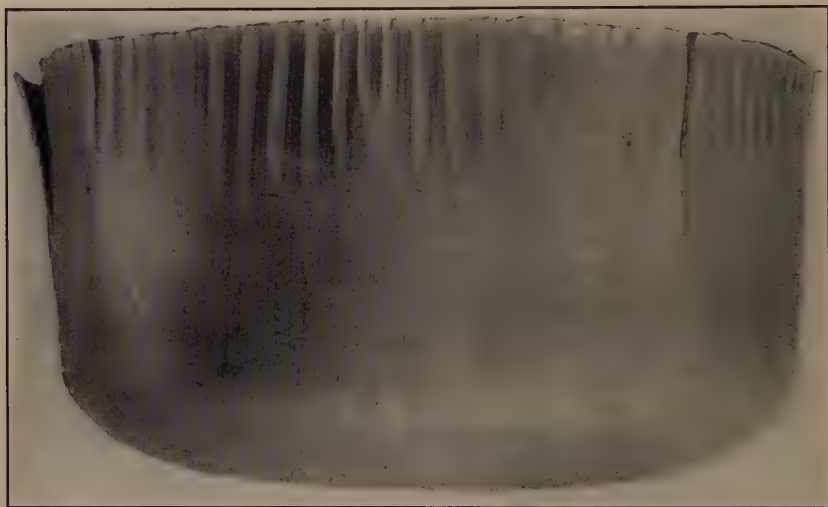


FIG. 1.—STRESS CORROSION OF COLD-WORKED ALUMINUM-MAGNESIUM (10 PER CENT MAGNESIUM) ALLOY.

that have made it possible for me to present this lecture today. I wish especially to mention my co-workers, W. L. Fink and L. W. Kempf, to whom belongs a large share of the credit for planning and coördinating the many laboratory investigations which have been necessary for an understanding of stress corrosion. It is our hope that the more important of these investigations will be published in detail later. I wish also to express my appreciation to R. B. Mears, R. H. Brown, G. F. Sager and J. J. Bowman, who have kindly aided in the preparation of this lecture.

MECHANISM OF INTERGRANULAR CORROSION

Any discussion of the metallurgical considerations that determine whether or not an alloy is susceptible to stress corrosion should, quite naturally, begin with the well recognized fact that, with few exceptions, the path of a stress-corrosion failure follows grain boundaries. This fact is of both theoretical and practical importance. Theoretically, it

furnishes an important clue to the mechanism of stress corrosion and, practically, it permits, by means of microscopic examination, a correct diagnosis of the cause of a service failure. Fractures produced by overloading, at room temperature, either by static or dynamic load, are, in most cases of industrial alloys, intragranular, as opposed to the intergranular nature of a stress-corrosion failure. The intergranular corrosion of metals and its relation to stress cracking or stress corrosion was discussed at some length in 1927 by Rawdon,¹⁴ who made the following significant statement: "The susceptibility of duralumin to this type of corrosive attack (intergranular) appears to be intimately related to the structural conditions obtaining at the grain boundaries as the result of heat-treatment procedures and mechanical treatment." In 1930, the late W. H. Bassett¹⁵ stated: "It has been our observation that there is a certain relation between dezincification and season cracking. We are not able to make an exact statement but, generally speaking, the brasses which dezincify or are subject to selective solution will season crack under what we may call ordinary conditions or atmospheric conditions. Those that are not subject to selective corrosion are much less liable to stress cracking." "Dezincification" is the brass man's name for a special type of corrosion, which is frequently intergranular.

A little over a decade ago L. J. Weber and I developed the essence of a theory to explain the intergranular corrosion of certain types of the heat-treated aluminum-copper alloys that have been either too slowly quenched or reheated after the solution heat-treatment. This theory was based on two facts, which will be discussed in some detail.

First, an understanding of the microstructural conditions that brought about susceptibility to this type of attack was obtained in 1926, when H. H. Richardson and I¹⁶ were able to show, for the first time by microscopic examination, the presence of discrete particles precipitated from an aluminum-copper solid solution by aging for two weeks at 200°C. subsequent to a solution heat-treatment. It was found that in all of the as-cast alloys with which we worked precipitation at the grain boundaries was in a more advanced stage than within the grains. Even when precipitation within the grains was indicated only by a mottled appearance produced after etching, the precipitate at the grain boundaries was readily resolvable and was found to be surrounded by narrow zones that etched smoothly. This condition is shown in Fig. 2. Since these results were obtained there has been considerable development, largely through the efforts of F. Keller, in the metallographic and etching technique applied to aluminum alloys. The important and convincing work of W. L. Fink and D. W. Smith¹⁷⁻²⁰ has confirmed these early indications in the aluminum-copper alloys. They have also found that similar conditions exist in aluminum-magnesium alloys and that in cold-worked sheet of both alloy systems the initial precipitation occurred along slip

planes as well as grain boundaries. Bain, Aborn and Rutherford²¹ have also concluded that carbide precipitation occurs at the grain boundaries of stainless steels that are sensitive to intergranular corrosion.

The second fact necessary for the theory was contributed by the work of J. D. Edwards and C. S. Taylor,²² who showed that, in chloride solutions, pure aluminum is electronegative to many of its alloys, particularly duralumin. They also found that aging at an elevated temperature, subsequent to a solution heat-treatment, changed the solution potential of a

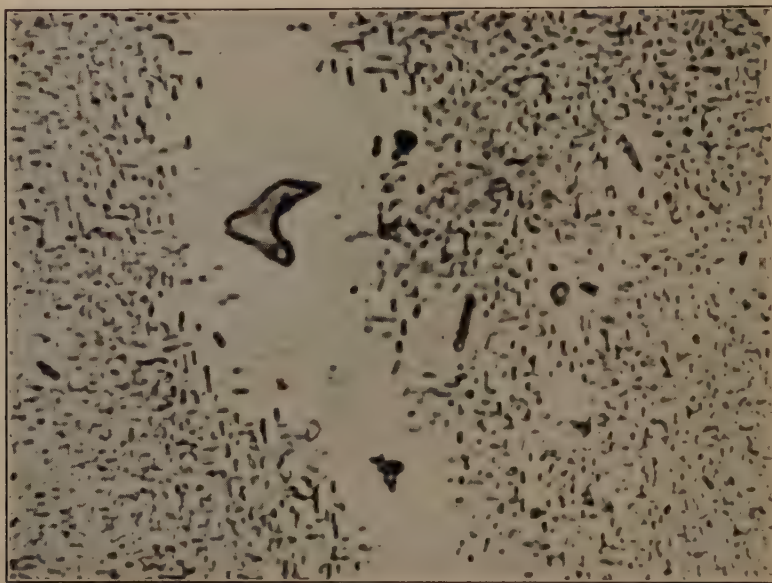


FIG. 2.—GRAIN-BOUNDARY ZONE IN ALUMINUM-COPPER (1.6 PER CENT Cu) ALLOY AFTER PROLONGED AGING AT 200°C. $\times 2000$. ETCH, 1 PER CENT NaOH.

duralumin-type alloy in the anodic direction, and they connected this fact with the lowered resistance to corrosion produced by such reheating.

Although the conception of Weber and Dix, previously referred to, was never published in detail, in 1928²³ the latter wrote as follows:

... our experiments regarding the solution potential of aluminum as compared to the alloy would indicate that there is a difference in solution potential between the material composing the grains and that at the grain boundaries, and that the direction of this potential would be such as to cause the solution of the metal at the grain boundaries to be greatly accelerated. The solution of the very small amount of metal in the grain boundaries would proceed rapidly and the corroding solution would be drawn by capillary attraction farther and farther below the surface, following always the films of purer aluminum along the grain boundaries. In this way, the strength and ductility of the alloy would be rapidly destroyed.

L. J. Weber and F. P. Somers,²⁴ continuing the work of Edwards and Taylor, found that, for a given piece of duralumin-type alloy, the sus-

ceptibility to intergranular corrosion as influenced by heat-treating conditions could be related to the solution potential of the alloy as measured in a sodium chloride-hydrogen peroxide solution. Such measurements have proved valuable in laboratory studies but are limited in their general applicability, as pointed out by J. B. Johnson.²⁵

F. Keller²⁴ found that particles of precipitate could be observed at the grain boundaries in duralumin-type alloys that had been made susceptible to intergranular corrosion, either by quenching too slowly or by reheating after a solution heat-treatment. Also, the contrast in etching characteristics between grains of different orientation was definitely less than in rapidly quenched material. Such microscopic indications have been valuable aids in differentiating between duralumin-type alloys that have been heat-treated so as to be immune to intergranular corrosion and those in which the heat-treatment has been such as to make them susceptible to this type of attack.

It has been shown²⁴ that, in chloride solutions, copper and silicon in solid solution in aluminum make the solution potential more cathodic. On the other hand, magnesium and zinc in solid solution make the solution potential more anodic. Thus, aluminum is anodic to aluminum-copper solid solutions, but cathodic to solid solutions of aluminum and magnesium. When magnesium and silicon are present in aluminum in the ratio of the compound Mg_2Si , a solution heat-treatment results in no significant change in the solution potential of the alloy. The numerical values obtained for the solution potentials of some aluminum solid solutions and intermetallic compounds are given in Table 1. These values agree remarkably well with those published by Akimow and Oleshko.²⁶ There is now considerable evidence to indicate that the first particles to

TABLE 1.—*Potentials of Aluminum Solid Solutions and Constituents^a*
NaCl-H₂O₂ Solution^b N/10 Calomel Scale

Copper.....	-0.20	MnAl ₃	-0.85
Silicon.....	-0.26	Aluminum containing 4 per cent	
CuAl ₂	-0.53	Mg in solid solution.....	-0.87
FeAl ₃	-0.56	Aluminum containing 4 per cent	
Aluminum containing 4 per cent		Zn in solid solution.....	-1.02
Cu in solid solution.....	-0.69	MgZn ₂	-1.04
Aluminum containing 1 per cent		Mg ₅ Al ₃	-1.07
Mg ₂ Si in solid solution.....	-0.83	Zinc.....	-1.10
Aluminum.....	-0.84		

^a R. H. Brown, Aluminum Research Laboratories.

^b 53 grams NaCl + 3 grams H₂O₂ per liter.

be precipitated in these systems do not have the same crystal forms as the compounds CuAl₂ and Mg₅Al₃ under equilibrium conditions. However, it seems reasonable to assume that the solution potentials of the transition

phases will not differ greatly from those of the equilibrium compounds. While it has not yet been possible to determine the solution potential of the compound Mg_2Si , it has been demonstrated, by corrosion experiments on surfaces that have received a metallographic polish, that there is no appreciable galvanic attack in chloride solutions between particles of the Mg_2Si constituent and the surrounding aluminum matrix. Hence its solution potential either does not differ appreciably from that of aluminum or polarization occurs so rapidly as to prevent any significant current flow. In similar experiments it was found that the aluminum solid solution matrix was corroded adjacent to the particles of the aluminum-copper compound CuAl_2 . In contrast, under similar conditions the particles of the compound Mg_5Al_8 , were corroded without affecting the surrounding aluminum-magnesium solid solution. Thus, these experiments confirm the potentials given in Table 1. It will be observed also that the potential of the compound MnAl_6 is approximately the same as that of pure aluminum. These facts undoubtedly account for the excellent resistance to corrosion of the aluminum- Mg_2Si and the aluminum-manganese alloys.

It is evident in aluminum-copper alloys that, if the thermal treatment has been such as to produce localized precipitation at the grain boundaries, the depleted solid solution zone adjacent to the precipitate will be anodic to the solid solution richer in copper within the grains and also to the particles of precipitate. Owing to the relatively small areas of these depleted zones, the current density will be high and the solution of these zones will be rapid. In the aluminum-magnesium alloys the situation is somewhat different. The particles of precipitate will be anodic to both the depleted solid solution and the solid solution richer in magnesium within the grains. Therefore, the particles of precipitate will be rapidly attacked.

To test the validity of the electrochemical theory of intergranular corrosion, R. H. Brown, working in collaboration with W. L. Fink and R. B. Mears, performed the following experiment. A piece of coarse-grained aluminum-copper (4 per cent Cu) alloy sheet was given a solution heat-treatment, followed by artificial aging, in order to put it in a condition susceptible to intergranular corrosion. Two specimens were then cut from this sheet. The grain boundaries of one of these were painted with Bakelite varnish so that only the grain areas would be exposed. The grain areas of the other specimen were masked out in a similar manner, so that only the grain boundaries were exposed. Of course, owing to the difficulty of the operation, the grain-boundary width was about 1 mm., which was greater than desired. The specimens were then immersed in a sodium chloride-hydrogen peroxide solution and measurements of open-circuit and closed-circuit potentials and of current flow between the two specimens were made in a manner shown schematically

in Fig. 3. The open-circuit potential of the specimens having the grain areas exposed to the electrolyte was -0.748 volt, and that of the specimen having the grain boundaries exposed was -0.792 volt. Thus, the grain boundaries were found to be anodic to the grain areas by 0.044 volt. Had it been possible to follow more closely the grain boundaries in the masking operation, the recorded difference in potential undoubtedly would have been greater. The closed-circuit potential of the two specimens joined electrically was -0.788 volt, which corresponds rather closely with the potential of the more anodic areas. For comparison, it may be noted that under similar conditions the solution potential of pure aluminum is -0.84 volt, and of the rapidly quenched aluminum-copper (4 per cent Cu) solid solution -0.69 volt.

While these potential measurements are of great interest and are in confirmation of the proposed theory of the mechanism of intergranular corrosion, the real measure of the amount of metal consumed by corrosion is the current that flows between the areas of high and low potential. Brown found that, in the aluminum-copper alloy specimens described, which were immersed in the solution so that the total exposed area of the pair of specimens was 56 sq. cm., the current was 2.1 milliamperes. The current density on the exposed areas of grain boundaries, therefore, is relatively high. The highly specialized technique required to make measurements of this sort has been described previously.^{27,28}

By a further development of this technique, Brown has succeeded in measuring the potential of very small local areas on the surface of the same aluminum-copper alloy. This was accomplished by using a small capillary tube drawn down to a diameter of 1 mm. A rubber tube connected this capillary tip to the calomel electrode. A drop of potassium chloride solution was permitted to flow through the tube and was held by surface tension to the capillary tip. This drop (about 1 mm. in diameter) was brought in contact with the surface of the alloy. The potentials obtained in this manner are shown in Fig. 4. These results confirm the previous findings in indicating that the grain boundaries are more anodic

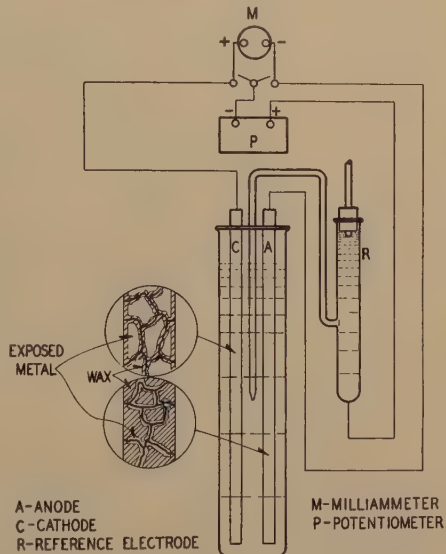


FIG. 3.—APPARATUS FOR MEASURING POTENTIAL AND CURRENT FLOW BETWEEN GRAIN BOUNDARIES AND GRAINS.

than the grains. They show also that the difference in potential between any grain and its boundary varies considerably and in some cases is as high as 0.20 volt. A further important fact is that the potentials of the centers of the grains also vary considerably. It was suggested that the measured potential may be related to the orientation of the grains as determining the number of copper atoms in the faces exposed to the electrolyte.

These electrochemical measurements, made on an alloy in which the susceptibility to intergranular corrosion is directly related to a heat-treat-

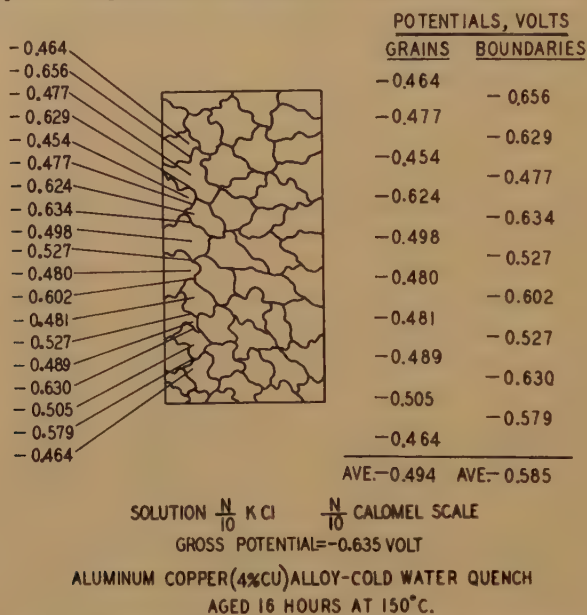


FIG. 4.—POTENTIAL OF GRAIN BOUNDARIES AND GRAINS.

ment that causes selective precipitation at the grain boundaries, indicate that, if similar painstaking measurements are made on alloys of other metals, the reason for their susceptibility to intergranular corrosion may be established and methods of prevention developed.

In the preceding discussion no mention has been made of the surface film that protects some metals from corrosion under many conditions. In environments in which the film is partially broken down, selective corrosion is likely to occur in alloys in which localized precipitation has occurred along grain boundaries (or, at times, slip planes) in an arrangement providing a more or less continuous path for corrosion to penetrate. Corrosion will occur along these pathways when the great volume of the material (the grains) is cathodic to the precipitated phase or the depleted zones adjacent to it. U. R. Evans²⁹ has discussed in further detail the electrochemical relations between the three different areas referred to and

the factors influencing the flow of current, with especial reference to the criteria set up by G. Akimow.³⁰

I have spent considerable time in discussing the intergranular corrosion of aluminum alloys, largely because I have had access to more complete data on these alloys. Perhaps it would be well, however, to take an example from another metal system. Bain, Aborn and Rutherford²¹ have attributed intergranular corrosion of stainless steel to the depletion of the chromium content of the solid solution at the grain boundaries caused by precipitation of chromium carbide. They feel that the corrosion along the grain boundaries is well accounted for by the lower resistance to corrosion of the impoverished iron-chromium solid solution.* It has been our opinion³¹ that the difference in solution potential between the depleted solid solution and the solid solution of higher chromium content within the grains was a contributory if not the main factor. It is known that low-carbon steel is strongly anodic to austenitic chromium-nickel steels, hence the depleted grain boundaries would be expected to be anodic to the grains. Hodge and Miller³² state:

Such intercrystalline corrosion (referring to austenitic chromium-nickel steels) is undoubtedly accelerated because of the presence of the resistant matrix and resistant chromium carbides in contact with the impoverished areas, thus establishing ideal conditions for the formation of an electrolytic couple.

In the examples just discussed the nature and the origin of the precipitated phase is known because of the large amount of investigation that has been devoted to these metal systems. In other cases the reason for selective corrosion at the grain boundaries is not so well understood, and many may seriously question whether precipitation is the only mechanism in wrought alloys by which significant differences in the solution potential of the grain boundaries as compared to the grains can be produced. Rawdon³³ has discussed the intergranular corrosion of extremely high-purity lead (99.99 per cent) in solutions of lead acetate and nitric acid. Another case in point is the discovery, by F. H. Rohrman,³⁴ that very high-purity aluminum rapidly quenched from a high temperature suffers intergranular corrosion in a 10 per cent HCl solution, whereas if slowly cooled, no preferential attack occurs. R. H. Brown,³⁵ applying the technique previously described, found that in aluminum sheet of 99.986 per cent purity quenched rapidly in cold water after being heated for 1 hr. at 620°C., the grain boundaries were anodic to the grains in a 20 per

* A. B. Kinzel has attributed the selective corrosion at the grain boundaries to strain and electrolytic effect increasing the rate of attack over the rate of formation of a passive film. He feels that chromium impoverishment is entirely unnecessary to account for the corrosion phenomenon. (Reference: discussion of paper by Bain and Aborn: Nature of the Nickel-chromium Rustless Steels. Amer. Soc. Steel Treat. (1930) 18, 875; Minute Nonferritic Particles in Steel. *Jnl. Applied Sci.*, 8, No. 5, May 1937.)

cent HCl solution and the measured current flowing from the grain boundaries to the grains was about 0.01 ma. On the other hand, in sheet slowly cooled from the same temperature, the grain boundaries were cathodic to the grains and the current flow was 0.09 ma. Clearly, the altered structural conditions brought about by different rates of cooling from the high temperature were responsible for a reversal in the solution-potential relations between the grains and the grain boundaries. Such behavior suggests a precipitating phase at the grain boundaries controlled by the rate of cooling even in this very high-purity metal.

INFLUENCE OF STRESS

So far in this discussion, little has been said about the effect of stress in accelerating the rate of corrosion. In stress corrosion the relative importance of the two factors—stress and corrosion—may vary over a wide range. Obviously, if a metal is stressed nearly to its breaking strength a very small amount of surface corrosion might be expected to initiate a crack. On the other hand, with stresses in the neighborhood of the yield strength or lower, a great deal of corrosive attack would be required to produce failure if there were not an interaction between stress and corrosion.

“Stress” may be defined as the unit internal force by which deformation is resisted. A condition of stress may be brought about by unequal deformation from part to part within the metal or by the application of an external load. The actual stress may vary greatly from point to point within the metal and in some locations may be much higher than the value calculated as load divided by net area. In fact, it seems likely that very small areas of a metal structure may be stressed nearly to the yield strength where the over-all average stress is much lower.

In most discussions of season cracking and stress corrosion, stresses induced by a condition within the metal (i.e., without external constraint) are referred to as “internal stresses.” This term is not really descriptive, since all stresses are “internal,” yet it has become accepted by common usage. More descriptive terms are “initial,” “locked-up,” or “residual.” None of these, however, seems sufficiently accurate to warrant adoption for this lecture. Such stresses may be produced by nonuniform deformation of the metal by cold-working, by unequal cooling from a high temperature, or by internal structural rearrangement involving volume changes. Stresses induced when a piece is bent, straightened or otherwise deformed (as, for instance, in the assembly of two poorly fitting parts), those induced by press and shrink fits, and in rivets³⁶ and bolts, may also be roughly classed as “internal stresses.”

These “concealed” stresses are often of greater importance in stress corrosion than the actual operating stresses for which the part was designed. Operating stresses, as taken into consideration in design, are

generally low enough to be of relatively little importance in the problem of stress corrosion except as they may be additive to the internal stresses. Design stresses are selected so as to avoid any permanent deformation in service and often are determined by the endurance limit of the metal. When the "factor of safety," required in the design of any structure to take care of unforeseen conditions in service, is added to the other limitations, the resulting stresses are almost always below a safe value as regards stress corrosion, providing the initial internal stress is not too high. Most workers in the field of stress corrosion have agreed that tension stresses approaching the yield strength of the metal are necessary to promote stress-corrosion cracking.

In the past the greatest amount of attention has been directed to cases where stress cracking is brought about by internal stresses with no external load applied. Thus, many papers have been written on the cracking of cold-formed brass articles such as cartridge shells. Stress cracking in tubing has also received much consideration.³⁷ The practical means of avoiding stress cracking in such articles is a low-temperature anneal carried out as a compromise between the desire, on the one hand, to relieve internal stress and, on the other, to retain sufficient strength and hardness. It has also been recognized, as pointed out by Crampton,³⁷ that fabricating processes involving cold-work can be carried out in such a way as to minimize the magnitude of the resulting stresses. For example, it is known that the sinking of tubing—drawing without the use of an internal mandrel—produces high stresses and should be avoided in materials susceptible to stress corrosion.

Stresses induced by internal structural changes are of great importance in relation to stress corrosion, especially so because such changes are often localized. When the reactions occur at the grain boundaries, high stresses may be induced microscopically in just those locations where corrosion may be greatest because of solution potential differences. It has been suggested⁴ that recrystallization occurring at the grain boundaries, with a local diminution of volume, would cause considerable intensification of stress, leading to the initiation of a crack. Fink and Smith conclude¹⁸ that in aluminum-magnesium alloys the "lattice parameter is not changed by precipitation of minute particles during age-hardening as it is by precipitation under equilibrium conditions." Since magnesium in solid solution in aluminum expands the lattice considerably, precipitation should result in contraction of the lattice. This apparently either occurs only in such highly localized areas as not to be revealed by X-ray diffraction methods or else the local contraction is restrained from taking place by the surrounding material. In either case, high localized stresses would be expected where precipitation has occurred at relatively low temperatures. In cold-formed material, precipitation occurs on slip planes as well as at the grain boundaries and

the same condition of stress probably exists on these planes. Stress-corrosion failures of such material often progress along slip planes as well as along grain boundaries.

Many investigators have studied the effect of the magnitude of the "internal" stress on the time required to produce stress cracking under a specific condition. In general, the magnitude of the internal stress has been calculated from measurements made on the change in shape of the article when the stress is relieved by machining.

The effect of quantitatively known stresses produced by applied external loads has received less consideration.* In 1921, Moore, Beck-

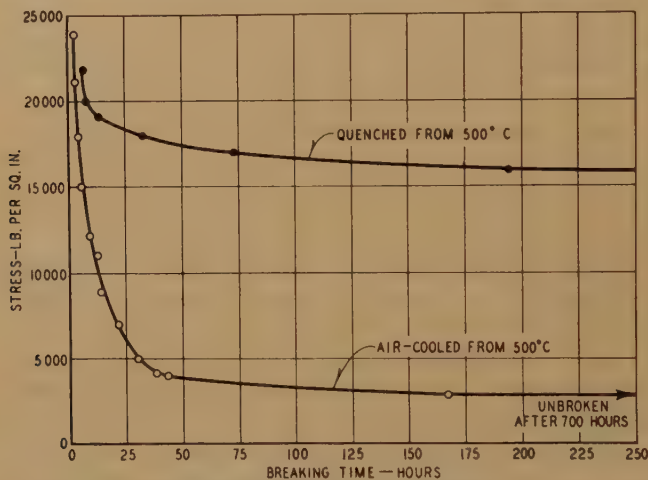


FIG. 5.—STRESS-TIME CURVES OF QUENCHED AND AIR-COOLED SAMPLES OF NAVAL BRASS (MORRIS⁴¹).

insale and Mallison³⁸ investigated the effect of known tensile stresses produced by an applied external load on the time to cause fracture in test pieces of 70-30 brass treated with a mercurous nitrate solution. They found that, in general, the time increased with decrease in stress and, within the limits of their test, fractures did not occur when the stress was less than 20 to 50 per cent of the tensile strength of the material. Parr and Straub,³⁹ in an extensive series of experiments beginning about 1926, stressed specimens of boiler steel by an externally applied load while subjecting them to the action of caustic solutions. Rawdon⁴⁰ stressed specimens of duralumin in tension and found that in certain

* In 1915, Ernst Jonson stressed hot-worked rods of gun metal, Naval brass, manganese bronze, Monel metal and aluminum bronze to 16,000 lb. per sq. in. (the calculated working stress) by means of dead-weight loads, and exposed them to the weather near the Ashokan Reservoir, New York, to determine whether these materials would stress-crack under such conditions. No cracks had occurred by 1918. (Discussion on corrosion cracking of brass. *Proc. Amer. Soc. Test. Mat.* (1918) **18**, pt. II, 203.)

corrosive conditions there was little, if any, acceleration of the rate of corrosion by a stress somewhat less than the yield strength. In 1930, Alan Morris⁴¹ studied the influence of externally applied stress on the time required to produce stress cracking in annealed brass. Of especial interest are his experiments on Naval brass quenched and air-cooled from 500°C., which are reproduced in Fig. 5. These indicate that quenching greatly increased the resistance of the alloy so that higher stresses were required to produce stress cracking. A similar effect of smaller magnitude was found for Muntz metal. This again illustrates the influence of thermal treatment on susceptibility to stress corrosion, probably by controlling precipitation.

In studies carried out at the Aluminum Research Laboratories on the effect of stress in accelerating the rate of corrosion of metals, several

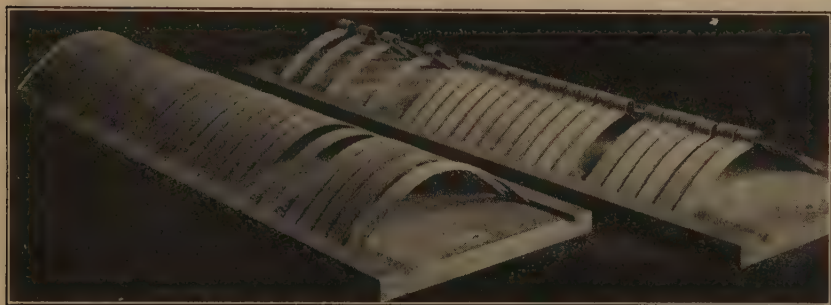


FIG. 6.—ELASTICALLY SPRUNG AND PREFORMED SPECIMENS FOR ACCELERATED STRESS-CORROSION TESTS.

different methods of applying stress by external loading have been used. The simplest of these stressing methods consisted in springing sheet specimens in the form of an arc and holding them in this position by suitable devices. This method of stressing has been used by many investigators but, as previously employed, had the disadvantage that the magnitude of the stress was unknown. A method by which the tensile stress in the outer fibers may be roughly controlled is shown in Fig. 6. In this case, the magnitude of the stress is controlled by the length of the specimen in relation to the distance between the two holding grooves.⁴² The specimens shown to the right of Fig. 6 have been plastically deformed with a U-bend in the center of the specimen prior to stressing.

In our early tests applying a known stress by means of a dead-weight load, a cantilever specimen of such shape that the stresses are constant over most of its length was employed. Following a method developed by R. G. Sturm,⁴³ it is possible to load the specimen to a stress within plus or minus 5 per cent of the desired value. In this test, the specimens were subjected to corrosion by immersion in a severely corrosive medium, generally a standard solution containing 53 grams sodium chloride and

3 grams hydrogen peroxide per liter. When a more accelerated test was desired, the specimen was made the anode in a 6 per cent sodium chloride solution with an applied potential of approximately 0.9 of a volt. Although the magnitude of the stress can be readily varied, the test offers only a single criterion of behavior, the specimen cracks or it does not. With such very severe corrosive conditions, it is sometimes difficult to tell whether the final failure is actually the result of stress corrosion or merely corrosion that has reduced the strength of the specimen so that it fails under the dead load it is carrying. Often the final decision can be made only after a microscopic examination to determine whether the crack is of the characteristic intergranular stress-corrosion type.



FIG. 7.—SIMPLE BEAM-STRESS CORROSION TEST, TOTAL IMMERSION.

For metals used as structural parts, it is important to know not only when a stress of a given magnitude will produce stress cracking but also whether stresses likely to occur in the operation of a part will accelerate the rate of corrosion in the environment to which the part is subjected. For the last fifteen years or so, it has been the practice in our laboratories to evaluate the effect of corrosion by determining the reduction in tensile strength and elongation of standard tensile specimens. These properties of specimens that have been exposed to corrosive conditions are compared with those of similar specimens that have been stored for the same period of time but protected against corrosion.

In order to determine the possible effect of known stresses of different magnitudes in accelerating the rate of corrosion, two types of tests were developed, one for sheet specimens and the other for cylindrical specimens. For the sheet tests, standard tension specimens were loaded as a simple beam at third points (Fig. 7), and totally immersed in a corrosive

solution. Several different methods of loading and of subjecting to corrosion were employed. In every case duplicate specimens were exposed in the same container without externally applied stress. Fig. 8 shows the method of dead-weight loading employed for atmospheric exposure; Fig. 9, the method of loading sheet tension specimens so that it is possible to subject them to alternate immersion. The latter method permits loading of the specimen by a dead load as in the previous test but uses also a locking device, so that once a specimen has been loaded to the desired amount by dead weights the loading plunger may be locked in place and the test conducted as a constant deflection test rather than dead load.



FIG. 8.—SIMPLE BEAM-STRESS CORROSION TEST, DEAD-WEIGHT LOADING, ATMOSPHERIC EXPOSURE.

The results of a test performed in this manner on sheet specimens 0.064 in. thick of the early aluminum alloy containing 20 per cent Zn and 3 per cent Cu, which Rosenhain and Archbutt³ found to be subject to stress corrosion, are shown in Fig. 10.⁴⁴ The tests were made on cross-grain, machined tensile specimens stressed as simple beams and exposed for 15 min. by alternate immersion in the standard sodium chloride-hydrogen peroxide solution. The stresses indicated are those to which the specimens were subjected by dead-weight loads, after which the deflection, corresponding to this stress, was maintained constant throughout the test. It will be observed that the stress produced by an external load has had little effect in accelerating the rate of corrosion, as indicated by the percentage of loss in tensile strength, below a value of about 50 per cent of the yield strength.

The method for loading cylindrical specimens (0.437 in. dia.) in direct tension is shown in Fig. 11. The stress is applied by forcing in the two



FIG. 9.—SIMPLE BEAM-STRESS CORROSION TEST.

Dead-weight or constant deflection loading, alternate immersion. Apparatus cover removed.



FIG. 10.—EFFECT OF STRESS IN ACCELERATING RATE OF CORROSION AS MEASURED BY LOSS IN TENSILE STRENGTH.

Early aluminum alloy (20 per cent Zn, 3 per cent Cu).

side members, which induces a tensile stress in the bar without the danger of torsional stresses, which would probably be caused if the nuts were

merely tightened. Knowing the stress deformation curve for the material under test, the desired stress is obtained by measuring the deformation with a sensitive extensometer. Throughout the test the deformation, rather than the load, is held constant. For total immersion, the specimen is surrounded by a container to hold a corrosive liquid (Fig. 12). Unstressed specimens similarly immersed may be observed in the second and fourth rows. This method of stressing is also convenient for other types of exposure such as salt spray, outdoor alternate immersion and atmospheric. In the development of these testing devices, the computation of stresses and the subsequent testing of the specimen, appreciation is expressed to R. L. Templin and members of his staff who worked in collaboration with W. L. Fink, C. M. Craighead and G. F. Sager.

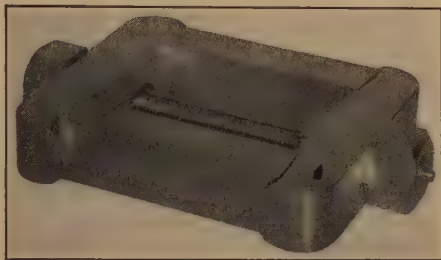


FIG. 11.—DIRECT TENSION STRESS-CORROSION FIXTURE.

INFLUENCE OF COLD-WORK

The part played by many types of cold forming in inducing high internal stresses—which, in turn, are responsible for most stress-corrosion



FIG. 12.—DIRECT TENSION STRESS-CORROSION TEST. TOTAL IMMERSION.

failures—has already been discussed. Simple cold-reduction operations as, for instance, in the cold-rolling of sheet, also have a pronounced effect in promoting sensitivity to stress corrosion in materials that have this tendency. The effect of cold-rolling in accelerating corrosion even without any stress induced by an externally applied load is strikingly illustrated by a series of aluminum-alloy sheet specimens (0.064 in. thick) containing 6, 8 and 10 per cent Mg, which were tested after different periods of exposure, up to 10 years, on the roof of the Aluminum Research

Laboratories at New Kensington, Pa. The change in tensile strength and elongation brought about by this extended exposure was small in the annealed sheet of the 6 and 8 per cent Mg alloy. Sheet of the 6 per cent Mg alloy that had been cold-reduced 50 per cent also showed only a small change in properties. The 8 per cent Mg alloy cold-reduced 50 per cent showed no appreciable losses after 2-yr. exposure. However, the effect of the cold-work in accelerating the rate of corrosion was clearly evident after 5-yr. exposure and at the end of 10 yr. this material had lost almost all of its tensile strength and elongation. The annealed aluminum alloy containing 10 per cent Mg had lost a considerably higher percentage of its tensile strength and elongation than the annealed alloys of lower magnesium contents. In this alloy the effect of cold-work was noticeable after the first year of exposure and after 2 yr. this material had lost substantially the same amount as the cold-reduced aluminum alloy containing 8 per cent Mg lost in 5 yr., and likewise the cold-reduced alloy containing 10 per cent Mg had lost as much in 5 yr. as the cold-reduced alloy containing 8 per cent Mg had lost in 10 yr. After 10 yr. exposure, none of the samples in this test showed any appreciable amount of surface corrosion but the cold-worked aluminum-magnesium alloys of the higher magnesium contents gave no metallic sound when struck a sharp blow and, of course, offered almost no resistance when tested in tension.

The corrosion of the cold-reduced sheet was intergranular, following planes parallel to the surface. Even in the annealed specimens, the edges that had been sheared subsequent to annealing had corroded intergranularly. The effects described may be attributed to induced stresses and different rates of precipitation during aging, the rates being greatly accelerated by the cold reductions and increase in magnesium content.

The following experiment is of interest in showing the acceleration of the rate of stress corrosion caused by plastically deforming annealed sheet. A number of sheet samples (0.064 in. thick) have been exposed, some on the roof of the Aluminum Research Laboratories and others to outdoor alternate immersion in a 3.5 per cent sea-salt solution in New Kensington for a period of over 5 years. Some of the samples were stressed by springing in the form of an arc in the manner shown in Fig. 6 while others were preformed as shown at the right of that picture and then elastically stressed in the same manner. Of 12 unpreformed specimens of an alloy in the annealed temper, containing about 7 per cent Mg and 0.3 per cent Mn, none have cracked in the New Kensington atmosphere, and of a similar number exposed in the sea-salt solution only two have cracked. However, 13 of the 14 preformed specimens have cracked in the New Kensington atmosphere in periods ranging from 300 to 1250 days, with an average period of 535 days, whereas of those exposed in the alternate immersion test, 12 of 14 have cracked in periods ranging

from 130 to 1030 days, with an average of 309 days. In the case of unpreformed specimens of the same alloy that had been given about 15 to 20 per cent cold reduction, 5 out of 10 exposed to the New Kensington atmosphere cracked in periods of 316 to 1931 days (average 1080) and all 10 exposed in the sea-salt solution cracked in from 211 to 1448 days (average 762).

THE INFLUENCE OF TIME

Time may play a dual role in stress corrosion. Corrosion attack progresses with time of exposure although, in the absence of stress, often at a decreasing rate. Also, structural changes such as precipitation proceed with aging time. Therefore, the time required for the alloy to reach an internal condition susceptible to stress corrosion should be considered separately from the time for a stress-corrosion failure to occur after this condition is reached. Often, however, these effects are overlapping. It has been found that some alloys, immediately after a heat-treatment or cold deformation, do not show susceptibility to stress corrosion in a standardized accelerated laboratory test; but if tested after aging at room temperature for 6 months or a year may have, in that interval, become markedly susceptible to stress corrosion as revealed by the same test. In the development of new alloy compositions this element of time considerably complicates the evaluation of the susceptibility of the new alloy to stress corrosion.

The rate of aging is increased by increasing the temperature above that of room temperature and, in consequence, long-time room-temperature aging effects can probably be duplicated in a relatively short time of storage at a somewhat increased temperature. It is well known, however, that elevated-temperature aging of some alloys produces susceptibility to intergranular corrosion whereas long-time room-temperature aging does not. Consequently, the device of using elevated-temperature aging to simulate room-temperature aging can only be employed with the greatest caution.

Fig. 13⁴⁵ illustrates the effect of aging at 100°C. to simulate long-time room-temperature aging on aluminum-magnesium (10 per cent Mg) alloy sheet annealed and cold-reduced 10, 20 and 40 per cent. The annealed sheet, which cracked when exposed to the salt spray in the form of elastically sprung specimens only after 510 days, when aged for 8 hr. at 100°C. cracked in 11 days in the same test. With only 10 per cent cold reduction the same material stress-cracked in 172 days when exposed in the same manner, whereas after 8-hr. aging at 100°C. it cracked in one day's exposure. With greater amounts of cold-work the times required for stress-corrosion failures are very much shorter even in the absence of aging. Aging, however, does accelerate the rate of attack, for, in the sheet cold-reduced 40 per cent, cracking occurred in 13 days but this time

was reduced to less than 7 hr. by aging 8 hr. at 100°C. The effect of room-temperature aging is illustrated by a cold-worked aluminum alloy containing about 7 per cent Mg and 0.3 per cent Mn.⁴⁶ This material tested soon after fabrication did not crack when stressed to three-quarters of its yield strength in a standardized electrolytic stress-corrosion test. However, after aging for 5½ yr. at room temperature it cracked in the same standardized test. In another test, bars of an experimental alloy stressed in direct tension to approximately the yield strength and subjected to total immersion in the standard sodium chloride-hydrogen

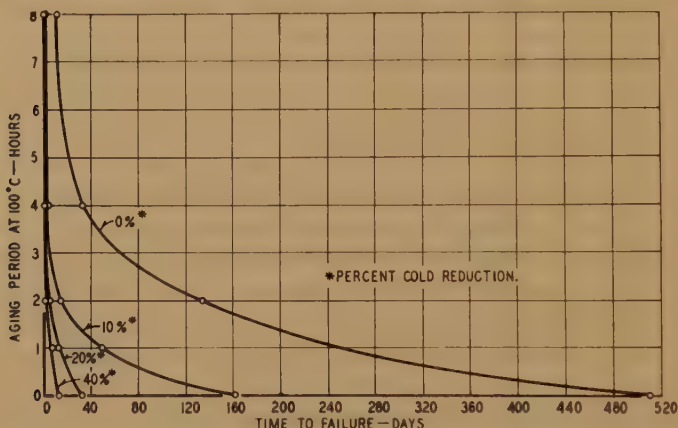


FIG. 13.—EFFECT OF COLD-WORK AND AGING ON TIME TO FAILURE IN ACCELERATED-STRESS CORROSION TEST.
Aluminum-magnesium (10 per cent Mg) alloy sheet.

peroxide solution after different periods of room-temperature aging failed in 52 hr. after 6-months aging, in approximately 15 hr. after 8-months aging, and in less than 1 hr. after 3½-yr. aging.

INFLUENCE OF COMPOSITION

In a treatise of this nature involving alloys of different metals the effect of composition cannot be discussed in any detail. The principles involved have been covered in the section on Intercrystalline Corrosion. Several examples will be given to illustrate the application of the testing methods previously described in studying the effect of composition on susceptibility to stress corrosion. R. H. Brown³⁵ has applied these methods to a series of brasses containing from 5 to 35 per cent Zn. Standard tensile specimens were loaded as simple beams to three-quarters of their yield strength and totally immersed in a solution containing 10 grams mercurous nitrate plus 5 c.c. concentrated nitric acid per liter. The curves of Fig. 14 show how the time required to produce cracking decreased with increase in zinc. In a 48-hr. exposure no cracks were encountered in the brasses containing less than about 15 per cent Zn.

In the higher-zinc alloys a low-temperature treatment to reduce the internal stress has increased the time required to produce failure in externally loaded specimens.

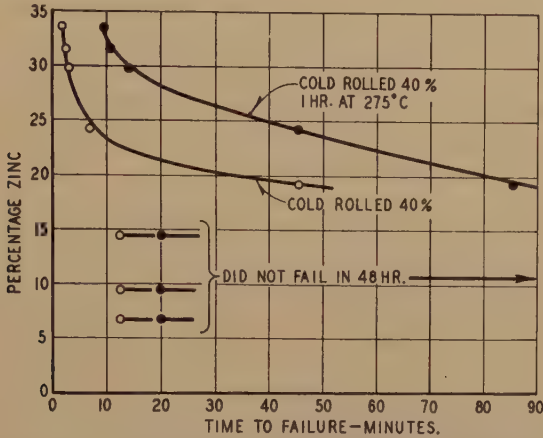


FIG. 14.—MERCURIOS NITRATE TEST OF BRASS SPECIMENS STRESSED TO 75 PER CENT OF YIELD STRENGTH.

Tensile specimens of the cold-worked sheet were also exposed without the application of external load. Specimens of compositions that did not crack were removed after 48 hr., and specimens of compositions that did crack were removed after the times required to produce failure.

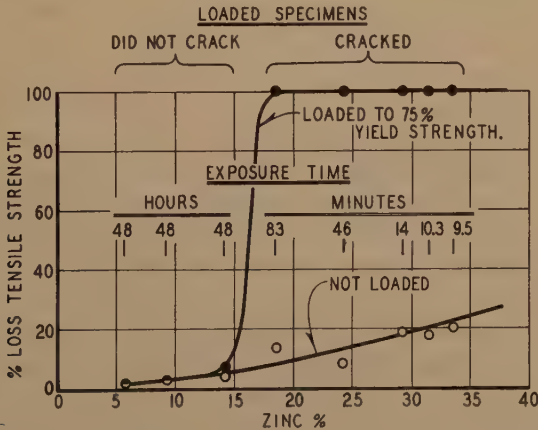


FIG. 15.—EFFECT OF STRESS ON RATE OF ATTACK ON COLD-WORKED BRASS.

The percentage of losses in tensile strength were obtained by comparing the tensile strengths of the specimens subjected to the mercurous nitrate solution with those of specimens that had not been so exposed. The results are plotted in Fig. 15. It will be observed that the percentage of loss in tensile strength in the specimens exposed without application of external load is relatively low. It is evident that corrosion in the

absence of external loading has not weakened the specimen sufficiently to account for the cracking that occurred.

The aluminum-magnesium alloys afford another interesting illustration. The results previously described confirm those of electrolytic stress-corrosion tests shown in the graph of Fig. 16.³⁵ These data were obtained on specimens of aluminum-alloy sheet of different magnesium contents cold-rolled 50 per cent and heated for 4 hr. at 100°C. to simulate long-time room-temperature aging. Uniformly stressed cantilever speci-

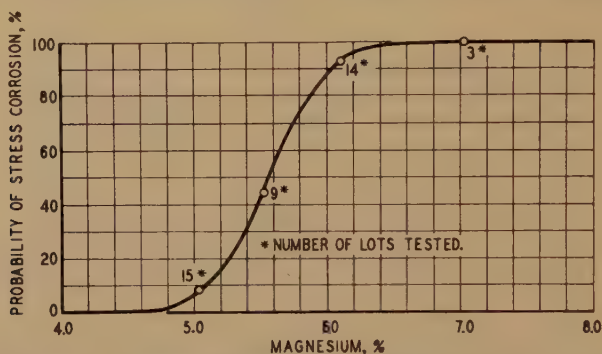


FIG. 16.—PROBABILITY OF STRESS CORROSION IN ACCELERATED TESTS OF COLD-WORKED ALUMINUM-MAGNESIUM ALLOYS.

mens were loaded by dead weight to three-quarters of the yield strength and totally immersed in the standard sodium chloride-hydrogen peroxide solution. A potential of 0.9 volt was applied in a direction to make the specimen the anode. Specimens that cracked under these conditions were considered susceptible to stress corrosion. The figures beside the points on the curve indicate the number of lots of material of the magnesium content indicated that were tested. The curve is a theoretical probability curve calculated on the basis of the experimental points. It shows that the probability of stress corrosion occurring in cold-worked sheet subjected to severely corrosive environment increases rapidly above about 5 per cent Mg.

In contrast to the unfavorable indications obtained on wrought aluminum-magnesium alloys containing more than about 6 per cent Mg when highly stressed, the alloys of lower magnesium content, say 5.25 per cent or less, possess remarkable resistance to corrosion, especially to salt water and salty atmospheres. Considerably higher magnesium contents are permissible in castings, where the upper desirable limit seems to be about 10 per cent Mg.

INFLUENCE OF CORROSIVE ENVIRONMENT

Stress-cracking in different metal systems is generally associated with some specific environments, such as ammonia in the case of brasses.

The mercurous nitrate test commonly employed in testing brass seems to be a special case, in which the action is somewhat like that of solders or other molten metals in producing intergranular cracks in stressed articles. Mercury will penetrate along the grain boundaries of many metals. Schroeder and Berk⁴⁷ have shown that the addition of small amounts of sodium silicate to sodium hydroxide solutions greatly accelerates the embrittlement of boiler steel. Copper sulphate solutions are employed in testing stainless steels. J. A. Jones⁴⁸ has shown that nitrates will, in a few days, stress-crack a medium-carbon steel that does not stress-crack in chlorides or sodium carbonate in 100 days. Many other examples have been given in the literature of metals that have corroded evenly and uniformly under one set of corrosive conditions whereas under another set of conditions corrosion has occurred rapidly at the grain boundaries and stress-cracking has resulted, often with very little surface corrosion.

Considerable evidence has been presented to show that intergranular corrosion is caused by the grain boundaries (either the precipitated phase or the depleted area surrounding it) being anodic to the grain areas in the corrosive environment to which the material is being subjected. It would be expected therefore that if this difference in solution potential could be overcome by an applied external potential or by altering the electrolyte so as to reverse the potential relations between the grain boundaries and the grains, stress corrosion could be prevented.

R. H. Brown³⁵ found that cold-worked aluminum-magnesium (10 per cent Mg) alloy specimens did not stress-crack even when stressed to three-quarters of the yield strength in a sodium chloride-hydrogen peroxide solution if an external potential of 0.9 volt was applied so as to make the specimen the cathode. When the circuit was broken the specimen cracked in the usual time, measured from the instant of the breaking of the circuit. General corrosion of the specimen occurred, presumably because of the hydroxide formed at the cathode. He also showed that, by adding 10 grams per liter of sodium hydroxide to the 6 per cent NaCl solution, the corrosion of the specimen was general and stress corrosion did not occur. Solution potential measurements showed that the addition of the sodium hydroxide had reversed the potential relation. Pure aluminum is cathodic to the aluminum-magnesium (10 per cent Mg) solid solution by 0.06 volt, which in turn is cathodic to the beta aluminum-magnesium constituent by 0.17 volt in the sodium chloride-hydrogen peroxide solution. However, in a solution of 6 per cent NaCl containing 10 grams per liter of sodium hydroxide, pure aluminum and the aluminum-magnesium (10 per cent Mg) solid solution were found to be anodic to the beta aluminum-magnesium constituent by 0.34 volt. This experiment is a strong confirmation of the electrolytic theory of stress corrosion.

Often stress corrosion occurs under such mild corrosive conditions that it is difficult to understand how corrosion could have influenced the failure. Several investigators have tried to prevent stress-cracking in metals known to be markedly susceptible to this condition, by attempting to protect them from corrosive influences. For instance, Grogan and Pleasance⁴⁹ found that the time required for failure of a specimen could be greatly increased by storing it in a vacuum. The following very interesting experiment was carried out by F. P. Somers and C. M. Craighead.⁵⁰

An experimental alloy stressed a few thousand pounds above its yield strength in direct tension cracked in a few hours in the sodium chloride-hydrogen peroxide solution and in 18 days in the atmosphere at New Kensington. The same alloy, stressed the same amount, was immersed in a neutral mineral oil (Nujol) and the time required to produce cracking was increased to 735 days. It was reasoned that the oxide film on the surface of the specimen had absorbed sufficient moisture between the time the specimen was machined and the time it was immersed in the Nujol to produce a mildly corrosive condition. Subsequently, a specimen of a similar alloy so susceptible to corrosion that one specimen stressed in direct tension to its yield strength failed in a few hours in the laboratory atmosphere, was machined under Nujol and kept covered while being stressed to its yield strength. It was then stored in Nujol and the time of failure was extended by these precautions to 1246 days. In our opinion, this experiment merely illustrates how difficult it is to completely protect against corrosive influences and offers a striking example of the effect of the corrosive environment on the time required for stress-cracking to occur. As a matter of fact, bars of similar alloys have been exposed on the roof of the Aluminum Research Laboratories for $6\frac{1}{2}$ yr. and none stressed less than about 60 per cent of the yield strength have cracked.

SIGNIFICANCE OF ACCELERATED STRESS-CORROSION TESTS

By the ingenious selection of the test conditions, it is probable that most metals in engineering use today can be made to fail by stress corrosion. To obtain results of practical value the test conditions must be selected with due regard to the service to which the metal will be subjected. Correlation between laboratory stress-corrosion tests and service performance is difficult to obtain and often requires many years. If the test conditions are intelligently selected, accelerated stress-corrosion tests are useful in the development of new alloys. The results of such tests on new alloy compositions may be compared with those obtained on established alloys whose performance over a number of years of service is known. In this way a comparative rating may be obtained and the probability of the new alloy failing in service by stress corrosion estimated with considerable accuracy.

PROCESS OF STRESS CORROSION

Stress corrosion of metals has been surrounded by mystery. The preceding discussion helps to explain why. There are many variables; only a few can be evaluated in any particular case. When the interacting effects of the various factors that have been discussed are considered, the process of stress corrosion is understandable. First, there must exist in the alloy a susceptibility to selective corrosion along more or less continuous paths as, for instance, at the grain boundaries. This susceptibility is present when the internal structure of the alloy is microscopically heterogeneous and the phase forming the continuous paths is anodic in the specific corrosive medium to the areas composing the major part of the structure. Second, there must exist a condition of high stress acting in a direction tending to pull the metal apart along these continuous paths. If these two conditions exist simultaneously and the metal is subjected to a corrosive environment producing the specified potential relations, corrosion will start along the anodic paths. This will produce a concentration of stress at the bottom of the notches so formed. As the stress increases, fissures will begin to develop, destroying any protective film and thus exposing fresh anodic material to the corrosive medium. Corrosion will proceed more rapidly and at the same time the stress will increase at an accelerated rate, especially if the material is subjected to a high external load. These mutually accelerated actions will continue at an increasing rate until the metal fails.

One of the curious aspects of stress-corrosion failures is the wide difference in the time required for failure, which varies from a matter of minutes to many years. There are several reasons for such wide variations. First, there is an incubation period in many alloys during which structural changes are occurring. Second, a long time may be required before corrosion proceeds to the extent that the rapidly accelerated process begins to act. It is obvious that the more severe the corrosive conditions and the higher the initial stress, the sooner this process will start.

Finally, failure of an alloy in accelerated stress-corrosion tests does not necessarily indicate that stress-corrosion failures are to be expected with it in practice. Experience has shown that in the absence of high internal stresses or excessively high stresses from external loading (often caused by faulty engineering), stress-corrosion failures are not encountered in service. This is even true of many alloys which, under the severely corrosive conditions used in accelerated tests, show an increase in their rate of corrosion when subjected to high stresses.

What, then, is the value of such accelerated tests as have been described? First, they enable the metal producer to determine which alloy compositions are markedly susceptible to stress corrosion under severely accelerated test conditions. Second, for alloys that are found to

be susceptible, the manufacturer may determine the fabrication conditions required to reduce or eliminate this tendency. Third, accelerated tests are useful as a means of technical control, to insure that the proper fabrication procedures are being consistently employed. Fourth, by studying the susceptibility to stress corrosion in accelerated tests, in comparison with that of alloys in general commercial use which have long and satisfactory service records, a decision can be reached on the use of any specific alloy composition for a given application.

It is important to recognize that many alloys that are subject to acceleration of rate of corrosion under high constant stress and corrosive conditions possess other valuable characteristics, often including high resistance to general corrosion. Such alloys have been extensively used commercially with satisfactory results for many years. It is clear, therefore, that there is nothing mysterious about susceptibility to stress corrosion; it is just another physical characteristic, which should be considered in the same light as such properties as endurance limit or yield strength in the selection of an alloy for a given application.

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Variation of Internal Friction with Grain Size

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(New York Meeting, February 1940)

THEORETICAL considerations by one of the authors have led¹ to the prediction that the dynamic internal friction of annealed metals has a broad maximum at a certain grain size. This prediction they have verified² for alpha brass. In the present paper the theory is extended to include the precise manner in which the internal friction varies with grain size on either side of the maximum. New experimental data are presented to test this extended theory.

The physical basis for the type of internal friction that is being investigated lies in the interplay between stress and temperature. Just as local fluctuations in temperature give rise to local fluctuations in stress, so likewise fluctuations in stress give rise to fluctuations in temperature. But temperature gradients give rise to necessarily irreversible thermal currents, and hence to internal friction. The theory for this type of internal friction has been developed quantitatively,³ and has been experimentally verified,^{4,5} for the particularly simple case of the transverse thermal currents accompanying transverse vibrations. Of more fundamental importance are the intercrystalline thermal currents accompanying all types of vibration. The variation in stress across grain boundaries arises from the elastic anisotropy and at least partial random orientation of the individual crystallites. An exact quantitative treatment of the internal friction due to these thermal currents is of course out of the question. However, much information can be obtained from general arguments.^{1,6} Thus when the frequency of vibration f is low, or when the grain size d is small, adjacent grains remain nearly in thermal equilibrium, and vibration proceeds isothermally with little internal friction. Again, when the frequency is high, or the grain size large, the heat flow per cycle is small, the vibration proceeds adiabatically with little internal friction. The internal friction will become a maximum in the transition region. The degree of adiabatic-

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¹ References are at the end of the paper.

ity can depend only upon frequency, grain size, and the thermal diffusion constant D , defined by

$$D = \frac{\text{thermal conductivity}}{\text{specific heat} \times \text{density}}$$

Since this constant has dimensions of length²/time, the internal friction can depend upon these factors only in the dimensionless combination fd^2/D . In their preceding paper² the authors have subjected this deduction to a rigid test by measuring the internal friction of annealed alpha brass over a wide range of grain size (0.006 to 4 mm.) and at several frequencies (6,000, 12,000 and 36,000 cycles per second). The internal friction was found in fact to be a function only of fd^2 . As the parameter fd^2/D increased from 0.005 through unity to 16,000, the internal friction increased from a very small value to a maximum, and again returned to a comparatively small value.

In the following section equally general arguments are presented showing that in the extreme isothermal case ($fd^2/D \ll 1$) this internal friction varies as the square of the grain size, while in the extreme adiabatic case ($fd^2/D \gg 1$) it varies inversely as the first power of the grain size. The comparative inaccuracy of grain-size measurements in the two extreme cases renders a direct experimental test difficult. However, this is not necessary, since this type of internal friction is a function of frequency and grain size only in the combination fd^2 . Hence a test may be made upon a *single* specimen by measuring the internal friction at several accurately known frequencies. In the extreme isothermal case the internal friction should be a linear function of d^2f ; in the extreme adiabatic case a linear function of $1/df^{1/2}$. Such a test is presented in this paper.

THEORY

The alternate extensions and compressions of a vibrating solid are associated with alternate lowering and raising of the average temperature. The inhomogeneities in stress between adjacent crystallites tend to superimpose upon this average rise and fall fluctuations that vary from grain to grain. On the other hand, thermal currents tend to equalize these temperature fluctuations.

We shall first show that in the extreme isothermal case ($fd^2/D \ll 1$) the density of these thermal currents is proportional to the grain size of the specimen. Through any point in the specimen we imagine drawn a closed surface, which, momentarily, is everywhere at the same temperature. The rate at which heat flows out of, or into, the enclosed region is such as nearly to maintain thermal equilibrium with the surroundings. We now imagine all microscopic linear dimensions of the specimen to be increased in the same ratio. The total flow of heat across the surface is

proportional to the volume of the enclosed region, and hence to the cube of the linear dimensions. But the area of the surface across which this heat flows is proportional only to the square of the linear dimensions. Hence the mean current density over the surface, as well as the actual current density in the vicinity of our original point, is proportional to the first power of the linear dimensions; i.e., to d . Now the rate at which the entropy of an elementary region increases is an even function of the thermal current density,* and so must be proportional to the square of the thermal current density, and hence to d^2 , provided this density is not too great. Finally, the internal friction of a specimen vibrating at constant amplitude is proportional to the rate at which heat is being generated, and hence to the rate of increase of entropy. It is therefore proportional to d^2 .

In the extreme adiabatic case ($fd^2/D \gg 1$) the flow of heat out of or into any region tends to vanish unless it is very close to another region with an appreciable temperature difference. The only regions so favorably located are in the immediate vicinity of the grain boundaries, across which the elastic constants change discontinuously. Hence the internal friction in this case is proportional to the total area of the grain boundaries. Since the number of grains in a unit volume is proportional to $1/d^3$, while the area of each grain varies as d^2 , we find that the internal friction due to thermal currents varies as $1/d$.

EXPERIMENTAL METHOD

The measure of internal friction used by the authors is Q^{-1} . This is $(1/2\pi)$ times the specific damping capacity. It is obtained either by observing the time τ required for the amplitude of longitudinal free oscillation to decay to one n th of its initial value, or by obtaining the ratio of the width Δf of a resonance curve at half maximum amplitude to

* An equation connecting the rate of increase of entropy with the thermal current density may readily be obtained. Let $(dq/dt) dv$ be the rate at which heat is flowing into an element of volume dv . Then

$$dq/dt = k\Delta^2 T$$

where k is the thermal conductivity and T the temperature. We obtain the rate of increase of the entropy of a system by dividing dq/dt by T and integrating over the volume of the system.

$$dS/dt = k \int T^{-1} \Delta^2 T dv.$$

The right-hand member of this equation may be transformed into two terms by means of Green's theorem. The first is the integral of $T^{-1}k \text{grad}_n T$ over the surface of the system. This gives the rate of entropy increase due to flow of heat into the system. The second term is the volume integral of $kT^{-2} (\text{grad } T)^2$; i.e., of $k^{-1}T^{-2}$ (thermal current density).²

the frequency f at maximum amplitude. In the former case

$$Q^{-1} = \log_e n / \pi \tau f$$

in the latter

$$Q^{-1} = 3^{-1/2} \Delta f / f.$$

The method of exciting and detecting vibrations is shown in Fig. 1. The specimen is supported by two horizontal silk threads at nodes of vibration, except for the first harmonic. For this harmonic the supports were within $1/20$ of a wave length from the one central node. This method of support is considerably more stable than the vertical loops used earlier² and is less liable to cause dissipation at the supports. The

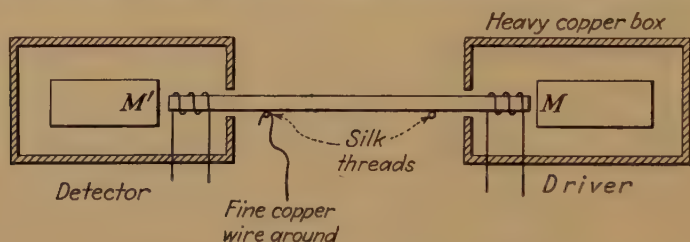


FIG. 1.—SIDE VIEW OF REED SUSPENSION.

driving force comes from the reaction of a magnetic field due to a permanent magnet M upon the eddy currents induced in the specimen by an alternating current in the driver coil. An electromotive force is induced in the detector coil by the eddy currents generated in the specimen by its motion in the magnetic field due to a second permanent magnet M' . In the previous experiments it was necessary to compensate for direct inductive feed-over between driver and detector, by means of a third coil connected to the source of power and opposing the field of the driver. In the present experiment improved shielding in the form of heavy copper boxes surrounding both driver and detector reduced inductive feed-over to a negligible amount. It was necessary to ground the reed at one of the points of support to avoid electrostatic coupling.

In the free-decay method values of n from 3 to 30 were used. The decay time was measured with an electrical stop clock in such a way as to avoid many of the errors in calibration of the amplifier system as well as the constant physiological timing errors. The stop clock was started as the amplitude of the decaying free vibration reached a predetermined value, as read on the amplifier output meter. The amplification was then quickly increased n fold by means of a calibrated potentiometer in the second stage of the amplifier and the stop clock stopped when the output meter read the same value as formerly.

The free-decay method gave good precision with the brass, where the time of decay was fairly long. With the zinc the higher internal friction

shortened the time of decay to the point where the resonance method became more suitable.

In order to eliminate possible frequency errors in calibrating the source of alternating driving voltage, the successive harmonics of the reeds were taken as a more reliable measure of relative frequencies. In the curves shown, therefore, the frequency has been plotted as exact integral multiples of the fundamental.

DATA AND DISCUSSION

Specimens of alpha brass were used in the investigation of the extreme isothermal case. These were the smallest grain-size samples of a set

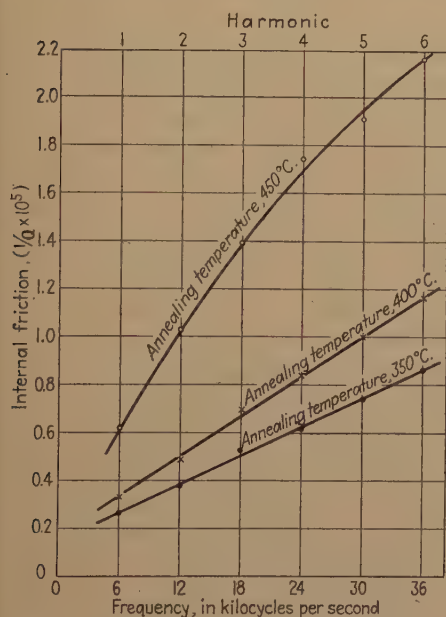


FIG. 2.—MEASUREMENTS ON BRASS SPECIMENS OF SMALL GRAIN SIZE.

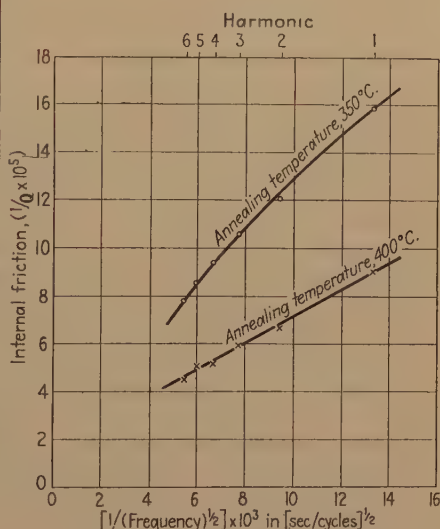


FIG. 3.—MEASUREMENTS ON ZINC SPECIMENS OF LARGE GRAIN SIZE.

furnished by C. S. Smith and E. W. Palmer, of the American Brass Co. Their preparation is fully described in reference 2. Their estimated grain sizes were 0.006, 0.009 and 0.015 mm., and their respective annealing temperatures 350°, 400° and 450° C.

Measurements taken at the first six harmonics of longitudinal vibration are plotted in Fig. 2 against frequency. Over this frequency range the measurements on the 350° and 400° C. anneal specimens lie upon a straight line within experimental error. The measurements on the 450° C. anneal specimen, of larger grain size, show an appreciable departure from linearity. This is associated with departure from the condi-

tion for nearly isothermal vibration, $fd^2/D \ll 1$. The theoretical linear variation with fd^2 in the extreme isothermal case implies that the slopes of the left-hand portion of these curves should be proportional to the squares of the respective grain sizes. The ratio of these slopes for the 400° and 450° C. anneal specimens is consistent with the grain sizes estimated by comparison with standard micrographs; namely 0.009 and 0.015 mm. Assuming these grain sizes to be correct, the ratio of the slopes of the 400° and 350° C. anneal specimens requires that the grain size of the latter be 0.007 mm., as compared with 0.006 mm. estimated by the standard method. The three experimental curves do not extrapolate at zero frequency to zero internal friction. The residual internal friction must be due to some cause other than thermal currents. Its value, about 0.15×10^{-5} for all three specimens, is very small compared with the maximum internal friction of 9×10^{-5} caused by intercrystalline thermal currents,² or with the maximum internal friction of 200×10^{-5} caused by transverse thermal currents accompanying transverse vibrations.⁴

Measurements over an extended frequency range have already been published² for the specimens with largest grain size (up to 4 mm.) of the same set of brass samples. These measurements do not vary in a linear manner with $1/f^{1/2}$, as is anticipated by the theory for the extreme adiabatic case $fd^2/D \gg 1$. The origin of this disagreement probably lies in the narrowness of the twin bands. These are so narrow that at the frequencies used the vibrations were not adiabatic in the interior of the bands. Thus although the internal friction was a surface effect as far as the intercrystalline thermal currents were concerned, it was a volume effect with respect to the flow of heat in and out of the twin bands.

The authors were fortunate in having suitable samples (dimensions $30 \times 1 \times 0.45$ cm.) of a second metal. These were the largest grain-size specimens of a set of zinc samples furnished by Gerald Edmunds, of the New Jersey Zinc Co., with a d of the order of magnitude of 0.3 mm. A description of this set will be given elsewhere, with a complete analysis of the internal friction.

The measurements are plotted in Fig. 3 against $1/(\text{frequency})^{1/2}$. Over the frequency range used the measurements on the 400° C. anneal specimen lie upon a straight line. The measurements on the 350° C. anneal specimen, of smaller grain size, show an appreciable departure from linearity. This is associated with departure from the condition for nearly isothermal vibration, $fd^2/d \gg 1$. The theoretical linear variation with $1/f^{1/2}d$ in the extreme adiabatic case implies that the slopes of the extreme left-hand portion of these curves be inversely proportional to the grain size. Hence, from these data alone, before grain counts have been taken, the authors can conclude that the ratio of the grain size of the 400° to the 350° C. anneal specimen is 2, the reciprocal of the ratio of the corresponding slopes. The extrapolated internal friction at $1/f^{1/2} = 0$ may

be regarded as the part of the internal friction that is not due to thermal currents.

SUMMARY

The internal friction arising from intercrystalline thermal currents is examined from a theoretical standpoint. It is found that in the extreme isothermal case of small grain size d this internal friction varies as d^2 , while in the extreme adiabatic case of large grain size it varies as $1/d$. These predictions may be tested by examining a single specimen over a range of frequencies of vibration.

Experimental data are presented which are in complete agreement with these theoretical predictions. It is found possible to estimate the part of the internal friction that does not arise from thermal currents. This residual internal friction is very small in the specimens examined. The relative grain sizes of specimens may be obtained from internal friction measurements with an accuracy comparable with that obtained from grain counts.

ACKNOWLEDGMENTS

In the preliminary part of this work, the authors were assisted by Mr. Irwin Wilson and Dr. Fred C. Rose.

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DISCUSSION

(E. E. Schumacher presiding)

R. SCHNURMANN,* Derby, England.—The extrapolation of a “residual internal friction” seems to be a serious consequence of the authors’ dimensional considerations. There is no evidence that the two curves, which are postulated to be straight lines, might not actually tend toward the origin at low frequencies, although the points measured in the frequency range of 6 to 36 kilocycles per second lie satisfactorily on a straight line. If the authors’ argument actually applied, the difficulty would arise of explaining the existence of internal friction, when the vibration frequency is zero.

The hypothetical “residual internal friction” is extrapolated by the authors to about 0.15×10^{-5} and compared with the maximum internal friction of 9×10^{-5} caused by intercrystalline thermal currents. Dr. Zener and his colleagues had measured this maximum of internal friction as a function of the grain size and established it for grain sizes between 0.05 and 0.2 mm. with vibration frequencies between 36 and 6 kc. per sec., respectively. For the present grain sizes of 0.009 and 0.015 mm., the

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internal friction measured with 6 kc. per sec. was found to be about 0.3×10^{-5} and 0.6×10^{-5} , respectively; i.e., only two to four times the value of the "residual internal friction."

R. L. WEGEL, * New York, N. Y.—It is remarkable that this explanation of energy degradation in solids, so long known in fluids, should have been so long delayed—no doubt because earlier workers had no means of experimenting with small enough strains. The authors are to be congratulated on their energy in carrying on this neglected problem of physics.

The paper states that internal friction, as measured by energy loss per cycle at a specified strain amplitude, when considered either as a function of the test frequency or of the surface area of a grain, should be linearly increasing for smaller values of the variable, then pass over a broad maximum, and finally decrease according to a square root law. It is also claimed that a quantitative theoretical treatment is impossible. The latter contention seems a little pessimistic, as it can be shown that the function described applies only to a material in which all "grains" are sharply defined, of substantially equal size, and have shapes in which the shortest dimension is not greatly different from the longest. Theoretical work on special hypothetical cases indicates also that laws other than those mentioned are possible. Similar considerations suggest that the grain boundaries are less likely to be responsible for the measured result than the differences in reaction of the various grains to stress. In a series of specimens of a metal having elongated grains or in which phase changes occur with or without crystal growth, quite different laws are to be expected. The authors seem to have made a good case for the proposition that most of the small strain friction in alpha brass is thermodynamic and that the "grains" are to be identified with the crystallites.

C. ZENER AND R. H. RANDALL (authors' reply).—The authors were not surprised at the existence of a residual internal friction that cannot be interpreted in terms of thermal currents. They had suspected that internal strains contribute to internal friction, as well as creep, particularly at high temperatures. These specimens were especially prepared to minimize these effects, but it could hardly be expected that the effects could be entirely eliminated.

The authors are glad of this opportunity to express their indebtedness to Dr. Wegel for advice on the technique of measuring internal friction. Their experimental method is, in fact, essentially that developed by Dr. Wegel in his own work on internal friction in metals.

R. F. MEHL, discussion on page 168.

* Bell Telephone Laboratories.

Changes in Damping Capacity during Annealing of Alpha Brass

BY JOHN T. NORTON,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

IN recent years, the damping capacity of metals has come to be recognized as an important index of certain types of structural change. In a number of instances, this property has proved to be particularly sensitive, but insufficient work has been done to permit a general interpretation. There is considerable question at the present time as to just what factors are responsible for the internal dissipation of energy when a metal is carried through a cycle of stress, and these factors must be ascertained if the value of the damping method as a metallurgical tool is to be determined. Since internal stresses are among the chief causes of dissipation of internal energy, or damping capacity, it was thought that a study of the changes in damping during the recovery and recrystallization of a cold-worked metal might throw some light upon the subject, particularly if the damping changes were correlated with other properties that are better understood. Probably more work has been done on the recrystallization phenomena of alpha brass than on any other metal, so this was chosen as the material for the present investigation.

Damping measurements on brass have been made by Förster and Köster.¹ They showed that the annealing of a brass that had been cold-drawn to 50 per cent reduction produced a rapid fall in the damping, a flat minimum occurring at approximately the temperature of recrystallization. The damping remained at a low value until grain growth was well under way and then it increased rapidly with increasing grain size. Köster and Rosenthal² continued the work in greater detail. They pointed out that the damping decrease does not correspond to the hardness drop but occurs at a lower temperature, suggesting that the relief or redistribution of internal stresses has a large effect while the actual recrystallization effect is small. They also show the increase in damping at the higher annealing temperatures. Their curves are reproduced in Fig. 1.

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* Associate Professor of Physics of Metals, Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

¹ References are at the end of the paper.

Their work closely parallels that of the present investigation but their method of measuring damping was quite different. They used extremely small stress cycles in bending at rather high frequencies, determining the damping from the resonance curve of the specimen. The present work employed very low frequency stress cycles in torsion with a wide range of

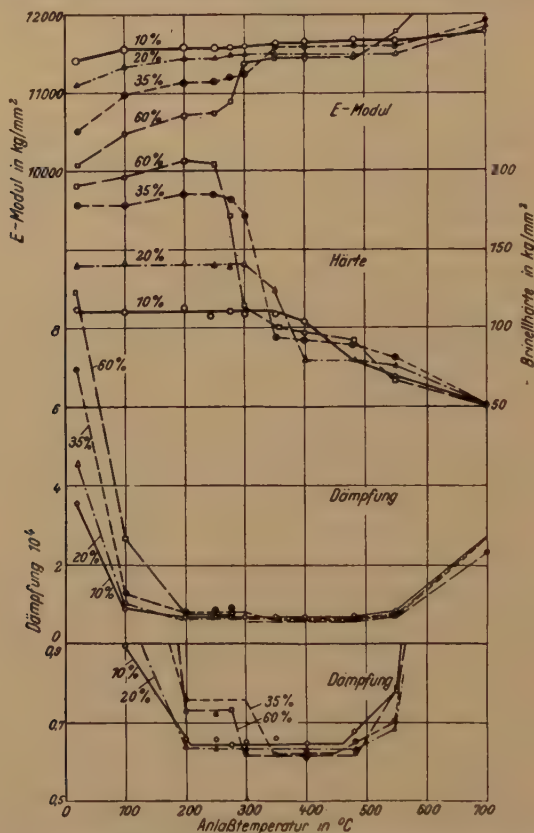


FIG. 1.—RESULTS OF KÖSTER AND ROSENTHAL'S EXPERIMENTS.²

Showing damping and hardness as a function of annealing temperature in cold-drawn brass.

stress, which in some tests exceeded the elastic range of the material. The results, however, are in general agreement.

Recently, Randall, Rose and Zener³ have published results showing that in stress-free samples of brass there is a proper combination of grain size and frequency at which a considerable damping is produced due to thermal currents set up by the elastic distortion of the grains. However, the frequency of the torsion pendulum system used in the present experiments was so low that the distortion process must be essentially an isothermal one and energy dissipation due to thermal currents cannot play any considerable part in the present results.

The problem thus resolves itself into two parts; one an observation of the damping changes that take place during the recovery and recrystallization, and the other an evaluation of the damping as an indicator of the internal stress and of the growth of the crystal grains. The experi-



FIG. 2.—TORSION PENDULUM DAMPING APPARATUS.

ments are of an exploratory nature and represent one of the preliminary steps in a detailed study of damping phenomena in metals.

EXPERIMENTAL PROCEDURE

The material used in the present work was a 70-30 brass of commercial purity (68.7 per cent Cu by analysis), supplied through the kindness

of Dr. Cyril Stanley Smith, of the American Brass Co. The annealed square bar was cold-drawn from 0.896 in. square to 0.750 in. square, giving a reduction in area of 31.5 per cent. Several months elapsed between the cold-working operation and the tests to be described, so that the material had come reasonably close to equilibrium at room temperature. The specimens for the damping tester were machined from the square rod.

The damping capacity of these specimens was measured by a modified torsion pendulum apparatus⁴ (Fig. 2). Briefly, it consists of a massive base in which is clamped the lower end of the specimen. This latter is a cylindrical rod with enlarged square ends to fit in the clamps. To the upper end of the specimen, an inertia bar is clamped, which is constrained to rotate about the axis of the specimen by a pivot system. The specimen

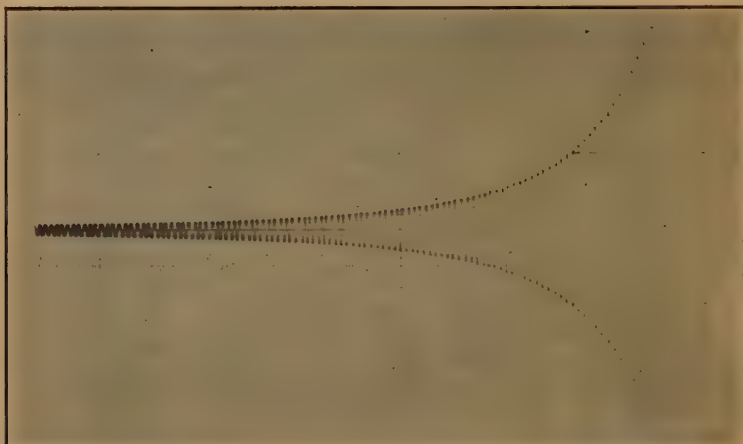


FIG. 3.—TYPICAL DAMPING RECORD.

is strained in torsion by rotating the inertia bar through the desired angle, where it is held by a pair of electromagnets. Upon the release of the magnets, the inertia bar describes a series of damped oscillations, using the specimen as the elastic element. The motion of the inertia bar is recorded by a rotating drum camera. The cylindrical portion of the test specimen was 4 in. long by 0.25 in. diameter. The moment of inertia of the inertia bar was such as to give a frequency of vibration of about 15 cycles per second. This frequency could be read directly from the damping record but no calculations of changes in the Coulomb modulus during annealing were made.

A typical record is shown in Fig. 3. From the amplitude of any cycle and the constants of the apparatus, one is enabled to calculate the surface strain or surface stress in the specimen. The difference in amplitude between two successive cycles is used to calculate the specific damping. Specific damping is defined as the ratio of the energy loss per cycle to the elastic potential energy at the maximum amplitude of the cycle, and

frequently is expressed in percentages. Other investigators, for instance Köster and Rosenthal,² have used the logarithmic decrement as a measure of the damping, and it is possible to show that the specific damping is almost exactly twice the logarithmic decrement, which makes a comparison of results quite easy.

A damping record such as shown in Fig. 3 enables one to calculate the damping at a number of different stresses. Since the damping is not constant for a range of stresses, but increases with increasing stress, the results on any one specimen are given by a curve of stress vs. damping rather than by a single value. This is an important consideration because equal specific damping at low stress does not mean equal values at a higher stress. In order to simplify the presentation of results in this paper, damping is expressed as a function of temperature, for several different stress levels, these points being taken from the individual damping curves.

One must be careful that the initial stress applied to the specimen does not produce a permanent twist, because even the slightest cold-working changes the damping. The safest procedure is to increase the initial stress by small increments, making a record of each run; when a point is reached where the lower parts of the curves no longer agree, it is a sign that the specimen has been overstrained. This also illustrates the difficulty of comparing the results on hard and soft specimens at the same stress level. It is hardly fair to compare one that is well within its elastic range with another that is stressed beyond this range and is deforming in a truly plastic fashion. But in spite of this difficulty, the ability to measure damping over a range of stresses is a real advantage because it is an indication of an important property of the material.

The reproducibility of the damping values on a single specimen is of the order of 5 per cent. The energy losses in the tester itself, including the air damping of the inertia bar, which is the largest item, correspond to a specific damping of less than 0.02 per cent.

In the as-received condition, separate specimens varied by something more than 10 per cent in their damping values. After recrystallization, however, the values come into much better agreement. For this reason it seems more significant to show the changes in a particular specimen at the various stages in the heating schedule. A similar procedure was used for the other property measurement. Duplicate specimens were run in all cases and the curves show the same shape and yield the same interpretation, although the numerical values at the beginning are slightly different. These differences are assigned to slight differences in the amount of cold-work the specimen had received before testing.

Electrical resistivity was measured on the cylindrical portion of the damping specimen after each step in the heating schedule by means of a Kelvin double bridge. The hardness was measured on the squared ends

of the damping specimen, the values given being averages of readings on both ends. The X-ray diffraction pictures were made on separate blocks cut from the 0.75-in. square bar and these blocks were heat-treated at the same time as the damping specimens. A back-reflection technique was employed, with a stationary sample and film, to show the changes in the width of the diffraction lines and the first appearance of new grains. These specimens were also examined microscopically.

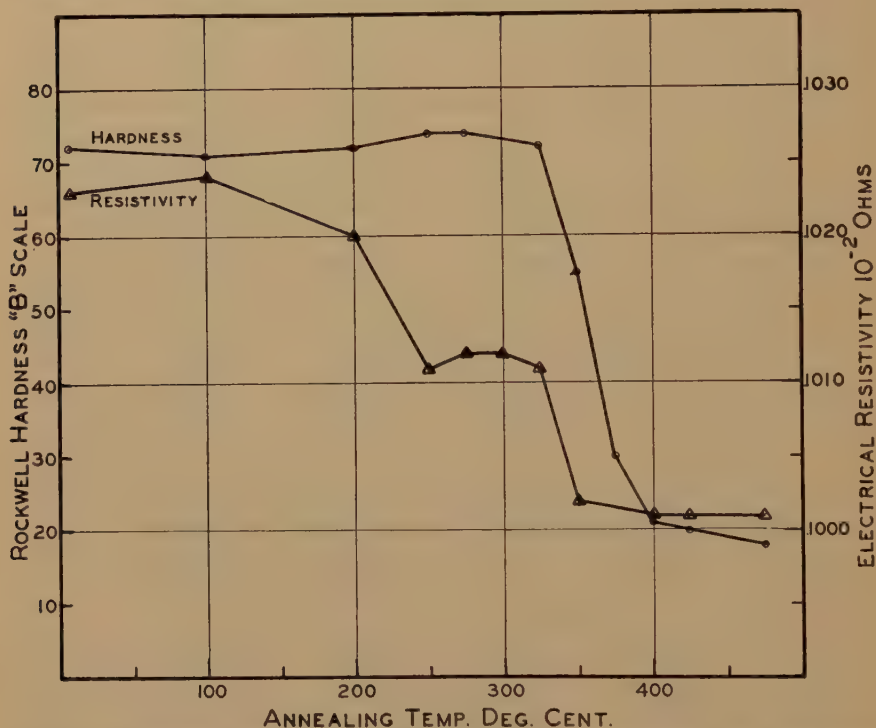


FIG. 4.—HARDNESS AND ELECTRICAL RESISTIVITY AS FUNCTIONS OF REHEATING TEMPERATURE.

Since it was desired to follow the behavior of individual specimens through the heating schedule, each specimen was examined in the cold-worked condition and then heated successively for one hour at each of the following temperatures: 100°, 200°, 250°, 275°, 300°, 325°, 350°, 375°, 400°, 425° and 475°C. After each temperature the specimens were air-cooled to room temperature and the observations were made.

RESULTS

The results of the observations on hardness, electrical resistivity and damping are shown as functions of reheating temperature in Figs. 4 and 5. The damping is expressed by a series of four curves, each giving the values at a particular stress level.

The hardness changes in exactly the manner to be expected, showing a gradual rise of a few points as the reheating proceeds, followed by a pronounced drop in the recrystallization range. After the drop is completed, further heating produces little change in hardness.

The electrical resistivity begins to decrease between 100° and 200°C., falling gradually to about 250°C. It then remains practically constant until 325°C. is reached, when another decrease occurs corresponding to

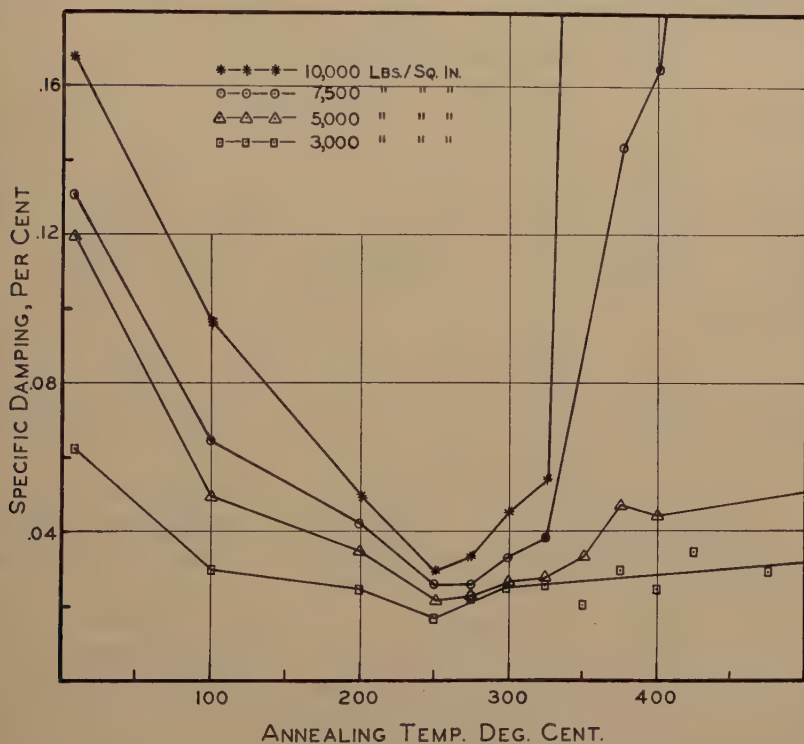


FIG. 5.—DAMPING AS FUNCTION OF REHEATING TEMPERATURE.

the drop in hardness. At the higher temperatures, the resistivity remains practically constant.

The damping curves show a decrease on the first heating at 100° and this decrease continues to the minimum point at 250°C. In the cold-worked sample, the damping is much greater at the higher stress levels, but at the minimum points of the curves, the effect of increasing stress is quite small. The minimum point of the 3000-lb. per sq. in. level corresponds to a damping value that is just about the energy loss in the damping tester itself and represents a sample that is almost perfectly elastic.

At the lower stress levels, the damping curves rise gradually with increasing temperature up to the limit of the range employed. At the higher stress levels, the curves rise abruptly at a temperature correspond-

ing to the drop in hardness, which is an indication that these stresses are beyond the elastic range of the brass in its soft state.

The X-ray diffraction results are summarized in Table 1. This indicates that the first evidence of grain growth or development of new grains is found at 325°C., while at 350°C. the recrystallization is well under way. It is also interesting that at the time when the first new grains appear there is still a background of very broad lines, showing no resolution of the alpha doublet.

TABLE 1.—*Results of X-ray Diffraction Pictures*

Temperature, Deg. C.	Condition	Temperature, Deg. C.	Condition
C. W.	Very diffuse lines.	325°	Diffuse lines plus a few spots.
100°	Very diffuse lines.	350°	Many spots on a slightly diffuse background.
200°	Very diffuse lines.	375°	Many spots on sharp background.
300°	Diffuse lines.	400°	Larger sharp spots.

DISCUSSION OF RESULTS

In planning these experiments it was hoped that it would be possible to use the well-known phenomena of recovery and recrystallization to explain the observed changes in damping. Possibly this implies a better understanding of these phenomena than is available at present. It would be extremely helpful if one could decide to what extent the measured damping is due to the presence of internal stresses and to what extent it is dependent upon the grain size. During recovery and recrystallization both of these factors change but the several other available methods of investigation are, to some extent at least, dependent on both factors. Only by a correlation of these observations can one expect to find an answer.

In the cold-worked brass one visualizes a structure made up of many small grain fragments and these fragments are elastically distorted by a system of heterogeneous elastic stresses ranging all the way up to the elastic limit of the material. The high values of the hardness, resistivity and damping, and the broad X-ray lines are all evidence of this condition, although it is difficult to estimate the relative influence of stress and of grain fragmentation.

It seems reasonable to suppose that the effect of low reheating temperatures upon the cold-worked metal would be confined primarily to the relief of the internal stresses. The damping shows by far the greatest change of any of the properties at this stage of the process. Köster and Rosenthal² showed that simply allowing the freshly cold-worked sample to stand at room temperature for periods of the order of 20 hr. reduced the damping to about one-half its original value. The

specimens used in the present work had come to equilibrium at room temperature but an hour at 100°C. produced a decrease of similar magnitude. The same treatment produced no measurable change in hardness or resistivity, which is clearly an indication of stress relief.

At a reheating temperature of 250°C., the damping reaches a minimum, and what is particularly important, it is low even for the highest stress level. This means that the sample is elastically fairly stable and suggests that the internal stresses are at a minimum, yet the hardness is at a maximum, the X-ray lines are diffuse and the resistivity has only begun to decrease.

The damping rises slowly and continuously from the minimum through the recrystallization temperature when the low stress levels are considered if this temperature is measured by the abrupt drop in hardness. At the higher stresses, the damping rises sharply coincident with the softening but this is merely an indication that the elastic range has been exceeded and the sample is being plastically deformed. This shows the value of testing the sample at several stress levels, for two samples might have identical damping capacities at one level but be entirely different at others. The gradual rise at 3000 lb. per sq. in. suggests that even this stress is slightly too high for the softened samples. Köster and Rosenthal showed no rise in this range when very low stresses were used.

An analysis of these results points definitely to the view that the principal source of energy dissipation in these experiments is due to a plastic deformation of the sample produced by the application of an external stress cycle. In the cold-worked material, the internal stress system cooperates with the externally applied stress to produce plastic flow in local regions. In the softened material, the larger values of external stress produce general plastic flow directly. However, in the state where the internal stresses are largely relieved, as after heating at 250°C., but the hardness is still high, the external stress is unable to produce any considerable plastic deformation, either local or general, and the damping is low. Thus, if the damping tests are properly carried out, the specific damping is a sensitive indicator of internal stress.

One point suggested by these results is of particular interest. If the damping indications of the presence of internal stress are accepted, the minimum point in the damping curve must represent the state of lowest internal stress. In the present experiment, this occurs at a somewhat lower temperature than the evidences of recrystallization. One might speculate on this basis as to the causes of the high hardness, the fairly high electrical resistivity and the broad X-ray lines at this temperature, if the stresses have been removed. There is the further question of just what happens when the hardness does drop and the X-ray lines sharpen, a phenomenon that has little effect upon the damping. Possibly these are phenomena in which stress plays a minor role, the fragmented grains

taking the lead. To carry the speculation a step further, one might suggest that the internal stresses in the cold-worked metal actually reduce the hardness produced by the very fine grain fragments, and that when the stresses are relieved the hardness rises. Such speculation is of little value when based upon the limited evidence presented here but suggests the importance of further work upon the subject. But if this further work establishes the fact that the damping observations will distinguish between the effects due to internal stresses and those due to fine grain sizes, an extremely useful tool will be made available for metallurgical studies.

SUMMARY

The present experiments confirm the fact that when metals are tested at comparatively low frequencies, the principal cause of energy dissipation is local or general plastic deformation. In cold-worked metals, the internal stress system is an important factor in the production of localized plastic flow. The relief of internal stresses by annealing reduces the damping to a low value and the value is low over a considerable range of applied stress. At the recrystallization temperature, the damping capacity shows little change, provided the applied stress is well within the so-called elastic range of the material. Considered from the point of view of a metallurgical tool, the damping capacity is a sensitive indicator of internal stresses but is relatively insensitive to changes in grain size.

ACKNOWLEDGMENT

The author desires to acknowledge the assistance rendered in these experiments by Mr. B. A. De Simone. The measurements were made by him as part of a senior thesis in the Department of Metallurgy, Massachusetts Institute of Technology.

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DISCUSSION

(E. E. Schumacher presiding)

G. SACHS,* Cleveland, Ohio.—There is the rather surprising point in Professor Norton's paper that low-temperature anneals cause a pronounced reduction of the specific damping, while the width of X-ray lines has been found to be little affected. Heretofore, both the increased damping and the broadening of X-ray lines caused by

* Assistant Professor, Metallurgical Department, Case School of Applied Science.

cold-work have been attributed to the same factor; namely, the presence of residual stresses. An anneal therefore should produce corresponding changes in these two properties. It would be interesting to know by what method the widths of the lines in the cold-worked brass were measured.

C. ZENER,* New York, N. Y.—Professor Norton has shown that annealing has the same qualitative effects upon the damping capacity measured at low frequencies as when measured at comparatively high frequencies. This suggests that the damping capacity associated with cold-working may be independent of the frequency^o used in measuring it. Of even more significance is his lack of correlation between hardness and damping capacity measured at high stress levels, which indicates that damping capacity has little connection with plastic flow, at least at room temperature.

Professor Norton states that the effect of increasing stress level is small at the minimum of his curves in Fig. 5. On the contrary, disregarding the part of the measured damping capacity that arises from apparatus losses, an increase of stress level may cause a greater percentage of rise in damping capacity at the minimum than to the left of the minimum. It is thus of interest to have measurements on similar material in which the apparatus losses are negligible. Such measurements, at very low stress levels, are given in Fig. 6, where it is shown that, at the minimum, the damping capacity of alpha brass measured at low frequencies and at a low stress level is less than 0.001 per cent. The specimens are completely described in reference 3.

The frequency variation shown in this figure is especially interesting. The damping capacity of the recrystallized specimens has been satisfactorily interpreted in terms of thermal currents flowing between adjacent grains, and the frequency variation has been found to be a sensitive indicator of the size of the grains.³ The frequency variation of the damping capacity of the specimens annealed 200° below the recrystallization temperature is more similar to that of specimens with 0.009-mm. grain size than to that of the original grain size of 0.06 mm. before reduction. This suggests that the low-temperature recovery is accompanied by the breaking up of the original highly distorted grains into smaller grains with perhaps less distortion. The initial drop in resistivity shown in Fig. 4 might be associated with this process.

S. E. MADDIGAN,† Waterbury, Conn.—It is interesting to compare the resistivity annealing curves given here with the results obtained by Maddigan and Blank (page 170, this volume). The results from the latter paper have been replotted in Fig. 7 as conductivity rise versus reduction in cross section. Depending on the grain size, the conductivity change after ½-hr. annealing at either 200° or 260°C. for 31 per cent

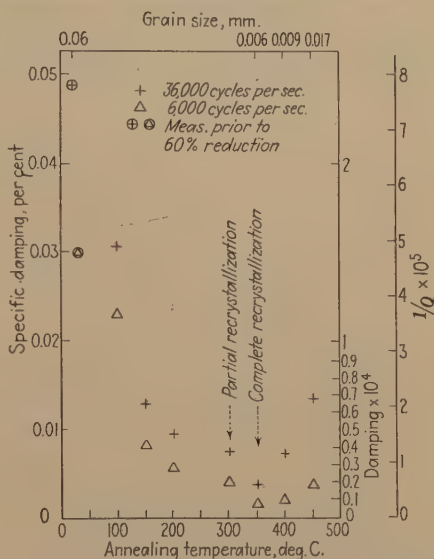


FIG. 6.—DAMPING CAPACITY OF ALPHA BRASS, NEGLIGIBLE APPARATUS LOSS.

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† Research Physicist, Chase Brass and Copper Co.

reduction is 1.9 to 3.6 per cent. After 5-hr. annealing, the change is 2.3 to 4.3 per cent. After complete annealing the change is 5 to 9 per cent, which is in good agreement with results of other investigators.*

The present report shows a change for complete annealing of only 2.5 per cent. Annealing for 1 hr. at 200°C. has produced a resistivity change of only 0.4 per cent.

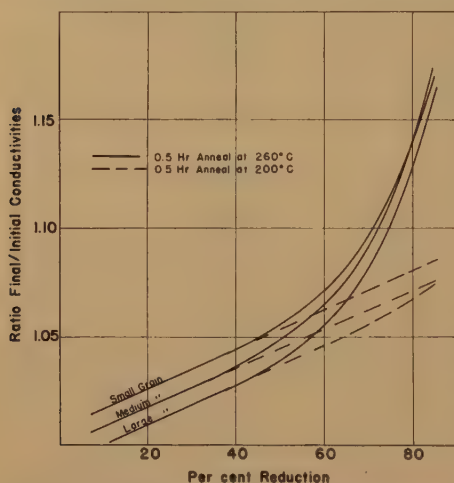


FIG. 7.—CONDUCTIVITY CHANGES FOR $\frac{1}{2}$ -HOUR ANNEALS AT 200°C. AND 260°C.

considerably smaller amount of working near the center of the bar, where both resistivity and damping measurements were made. No clue to this could be given from the Rockwell hardness values, as these were made on the square unmachined ends of the bar.

The steep slope of the curve occurring between 200° and 250°C. rather than at lower temperatures may be due to the presence of impurities, and it would be of value if the author would present an analysis of the alloy. The phenomenon might also be explained if any unusually large grains exist in the specimen.

N. P. Goss,† Youngstown, Ohio.—Professor Norton says that in cold-worked brass the high values of hardness, resistivity, damping, and broad X-ray lines indicate the presence of heterogeneous elastic stresses, ranging all the way up to the elastic limit of the material. In my opinion, the hardness of any metallic aggregate is related to the particle size, or grain size. Cold-working an annealed metal simply fragments the grains into smaller crystallites, which differ in size and orientation from each other and the parent grain, and, in a sense, may be looked upon as new grains produced by mechanical means. The smaller the grains, or crystallites, become, the greater the resistance to further deformation and the harder the metal, which after all is only a measure of resistance to further deformation.

Wood has recently shown that grain fragmentation does not proceed without limit, but that there is a lower limiting value of the order of 10^{-5} cm. This explains why the most drastic cold-working does not harden a metal as much as other means.

When a single crystal is cold-worked, new crystallites are produced and therefore more internal surface. The spacing between the displaced crystallites must increase

On further annealing for 1 hr. at 250°C., a change of 1 per cent occurs, giving a total change of 1.4 per cent. Thus, the course of the resistance-temperature curve is not in agreement with the results of Maddigan and Blank, nor is the total resistance change in agreement with accepted values.

Some doubt exists concerning the values reported in the curves for electrical resistivity. The value of resistivity for annealed alpha brass is about 7×10^{-6} ohm-cm. For the dimensions given in the paper, the resistance of the specimen should therefore be 2×10^{-4} ohms.

It is known that the working of the metal during the drawing of a square bar of the size used here is not uniform, therefore we might expect a

* Guillet and Ballay: *Compt. rend.* (1923) **176**, 1800.

† Director of Research, Cold Metal Process Co.

since work has been done in fragmenting the grains, and has created new orientation relationships. This requires an increase in the potential energy and demands a slight increase in the spacing between the displaced lattice blocks. Suppose that a large single crystal of iron is deformed. Slipping will take place by rotation on the $\{110\}$ planes. Before slipping the spacing of the $\{110\}$ planes is the same throughout the crystal; after slipping, the adjacent lattice blocks are rotated with respect to each other, and this causes the spacing between the displaced lattice fragments to increase.

X-rays cannot detect or measure this change in spacing. Since this occurs on many thousands of slip planes a slight decrease in density is to be expected.

Line broadening, in view of results obtained by myself and others, indicates that it must be associated with particle size, and not internal stresses. It should be pointed out that X-ray technique can be responsible for spurious line broadening unless certain precautions are exercised.

R. F. MEHL, discussion on page 168.

An Electron Diffraction Study of Anodic Films

By R. A. HARRINGTON* AND H. R. NELSON†

(New York Meeting, February 1940)

THE structure of anodic films formed on aluminum and other metals under varied conditions is not well known despite the wide use of such films both as protective coatings and as the dielectric medium in electrolytic condensers. The present work was undertaken as a survey of the possibilities of electron diffraction in the investigation of anodic films, especially in comparing the properties of anodic films formed under different sets of conditions and subjected to various subsequent treatments. In addition, an effort has been made to compare surface films formed on aluminum by anodic treatment with surface films formed by heating, immersion in chemicals, etc. The electron diffraction method in many cases has been successfully applied to the study of thin surface films. Its principal advantage is that it can be used without removing the films from the base material upon which they have been formed. The low penetrating power of electrons, in the "reflection" diffraction method which has been used in this work, prevents the appearance of diffraction patterns from substances at depths greater than about 100 Ångstrom units (10^{-6} cm.).

Different investigations of the structure of anodic films have shown widely varying results, depending on the methods used in preparing the films. Apparently under some conditions these films are crystalline and under other conditions they are amorphous, and it has been difficult to say which type of structure will be found in any particular case. Schmid and Wassermann's¹ X-ray diffraction patterns of cloxal‡ films show two broad, diffuse bands, which these investigators attribute to finely divided cubic γ - Al_2O_3 .§ Burgers, Claassen, and Zernicke³ obtained sharp X-ray

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† Battelle Memorial Institute, Columbus, Ohio.

¹ References are at the end of the paper.

‡ The product of a German commercial process for protective anodic coating of aluminum in an oxalic acid bath.

§ The maxima of the bands correspond closely with the electron diffraction maxima obtained by Preston and Bircumshaw² from an amorphous oxide film formed on aluminum in air.

patterns from anodic film material formed on aluminum, titanium, tantalum, and zirconium, showing that the films were crystalline in structure. They concluded that their film on aluminum, formed in a boiling electrolyte of borax-boric acid solution, consisted of γ - Al_2O_3 . From a further analysis of their results Verwey⁴ concluded that this film consisted of a modified γ - Al_2O_3 which he named γ' - Al_2O_3 . Belwe⁵ obtained electron diffraction patterns by transmission through extremely thin anodic films; these showed two moderately sharp rings. Belwe's films that had anodic treatment of more than a few seconds' duration were too thick to transmit electrons; by "reflection" technique these showed diffuse patterns of apparently random scattering.

The greater part of the present work is concerned with anodic films formed on aluminum in a number of different electrolytes, and with the effects of sealing and heating treatments on these films. The results of anodic treatments of other metals, including titanium, tantalum, chromium, nickel, copper and iron, are compared with those for aluminum. Films formed by immersing aluminum in hot chemical solutions are compared with results of the anodic process.

PREPARATION OF ANODIC FILMS

Specimens of aluminum and other metals* were given anodic treatments in a number of different electrolytes, some of which were used both at room temperature and at boiling temperature. The specimens were cut to such a shape that they would fit conveniently into the electron diffraction apparatus. Each had one flat face with an area of about one square centimeter, polished either with grade 0000 emery paper or with a fine abrasive (alumina or magnesia) on a wet polishing wheel. Each specimen was provided with a handle, usually of its own material, by which it could be suspended in the electrolyte. Anodic treatment was carried out in a 400-c.c. beaker containing the electrolyte and a platinum cathode, while a glass motor-driven stirrer agitated the solution. Immediately after anodic treatment each specimen was rinsed with distilled water, alcohol and ether. Care was taken not to contaminate the surface with grease or nonvolatile matter. Diffraction patterns were obtained both before and after anodic treatment.

The conditions of treatment for the specimens are given in Table 1. The voltage given represents the maximum or final voltage across the cell; often the voltage was raised slowly to this value to avoid excessive currents. The initial current density† given is the highest during the

* The aluminum specimens of 99.95 per cent purity were supplied by the Aluminum Research Laboratories of the Aluminum Company of America, through the cooperation of Dr. W. L. Fink. Specimens of other metals were of commercial purity.

† The current densities given are probably in error because of a tendency toward high current concentration on the handle of the specimen at the electrolyte

treatment. The table shows that some of the anodic films were highly resistant to electrolysis, since high voltages were required to pass small currents. Examples are the films formed on aluminum in borax electrolytes, and the films formed on tantalum. Such films are the basis of commercial electrolytic condensers, and they possess rectifying properties that have been used commercially. The highly resistant films are always very thin. Thicker films, formed on aluminum in electrolytes such as sulphuric and oxalic acids, are useful for protection of the metal against corrosion and abrasion. Still other electrolytes, such as potassium hydroxide, do not build up protective or resistant films on aluminum because they can dissolve anodic film material rapidly.

Other metals not listed in the table were given anodic treatments. Chromium did not build up a resistant film in $\frac{1}{2}$ normal boric acid. Three specimens of nickel, treated anodically in $\frac{1}{2}$ normal solutions of phosphoric acid, oxalic acid, and sodium carbonate did not build up resistant films. A copper specimen, given an anodic treatment in $\frac{1}{2}$ normal potassium ferricyanide, developed a thick brown film of crystalline material, probably cupric ferricyanide. Iron specimens treated anodically in sodium hydroxide and sodium sulphide solutions developed no protective or insulating film.

ELECTRON DIFFRACTION APPARATUS

The electron diffraction apparatus is similar in design to that of Thomson and Fraser,⁶ especially in the construction of the motions adjusting the position of the specimen. A hot-filament source of electrons replaces Thomson and Fraser's discharge tube, and lantern slide plates are used in an improved plate magazine following closely the design of Yearian and Howe.⁷ The electrons are accelerated by a 35-kilovolt potential rise from cathode to anode; this is supplied by a mechanically rectified unit with an 0.01 microfarad condenser in shunt. The electrons have a de Broglie wave length of 0.064 Å. The "reflection" diffraction method is used with a specimen-to-plate distance of 40.5 centimeters.

DIFFRACTION PATTERNS OF ANODIC FILMS

The most important diffraction patterns, including a few that are typical of a large group of electron diffraction exposures, are represented schematically in Fig. 1. The diagrams of this figure represent by their abscissas the positions of the observed diffraction maxima, and by their ordinates the relative diffraction intensities, estimated visually. Broad diffuse bands are represented by squat curves, and sharp rings by vertical lines. The scale of the figure is such that the distances between curves

surface. The values may still be taken as a relative indication of the insulating properties of the film.

TABLE 1.—*Conditions of Anodic Treatment*

Specimen—Reference to Figure	Polishing Agent	Electrolyte	Voltage	Current Density, Milliamperes per Sq. Cm.		Temperature, Deg. C.	Duration of Anodic Treatment, Min.
				Initial	Final		
$\left\{ \begin{array}{l} 1-A \\ 2 \end{array} \right\}$ 99.7 per cent Al ^a	MgO	0.5 N H ₂ SO ₄	22	7	7	25	25
^b 99.7 per cent Al ^a	MgO	70 per cent H ₂ SO ₄	7	13	13	31	20
^b 99.7 per cent Al ^a	Al ₂ O ₃	0.5 N H ₃ PO ₄	100	7	1	25	25
^b 99.7 per cent Al ^a	MgO	0.1 N Na ₃ PO ₄	120	13	7	26	30
1-B 99.7 per cent Al ^a	MgO	16 grams per liter borax	120	7	<1	26	20
^b 99.7 per cent Al ^a	MgO	0.25 M NaHCO ₃	120	7	<1	27	20
^b 99.7 per cent Al ^a	MgO	0.1 N Na ₂ CO ₃	120	17	4	28	20
^b 99.95 per cent Al ^a	MgO	0.5 N Oxalic acid	40	8	8	29	30
^b 99.95 per cent Al ^a	MgO	0.5 N NH ₄ OH	25	11	11	29	20
3 99.95 per cent Al ^a	MgO	0.5 N H ₂ SO ₄	3.5	45	45	98	15
$\left\{ \begin{array}{l} 1-C \\ 4 \end{array} \right\}$ 99.95 per cent Al ^a	MgO	$\left\{ \begin{array}{l} 100 \text{ grams per liter H}_3\text{BO}_3 \\ 2 \text{ grams per liter borax} \end{array} \right\}$	500	2	0.7	99	90
1-G Ti.....	0000 emery	0.5 N H ₃ PO ₄	75	41	20	98	60
1-E Ti.....	0000 emery	0.5 N H ₃ PO ₄	110	14	2	26	60
1-F Ta ^c	0000 emery	$\left\{ \begin{array}{l} 100 \text{ grams per liter H}_3\text{BO}_3 \\ 2 \text{ grams per liter borax} \end{array} \right\}$	200	1.6	0.5	99	90
^b Ta.....	0000 emery	40 grams per liter H ₃ BO ₃	95	0.2	0.2	26	15

^a The specimens of 99.7 per cent Al were used before the 99.95 per cent specimens had been obtained. Electron diffraction results on specimens of each purity after anodic treatment in sulphuric acid solution showed no significant differences.

^b Specimens which after anodic treatment had diffuse diffraction patterns similar in appearance to Fig. 2.

^c Sheet of tantalum from which a diffraction specimen was cut after anodic treatment.

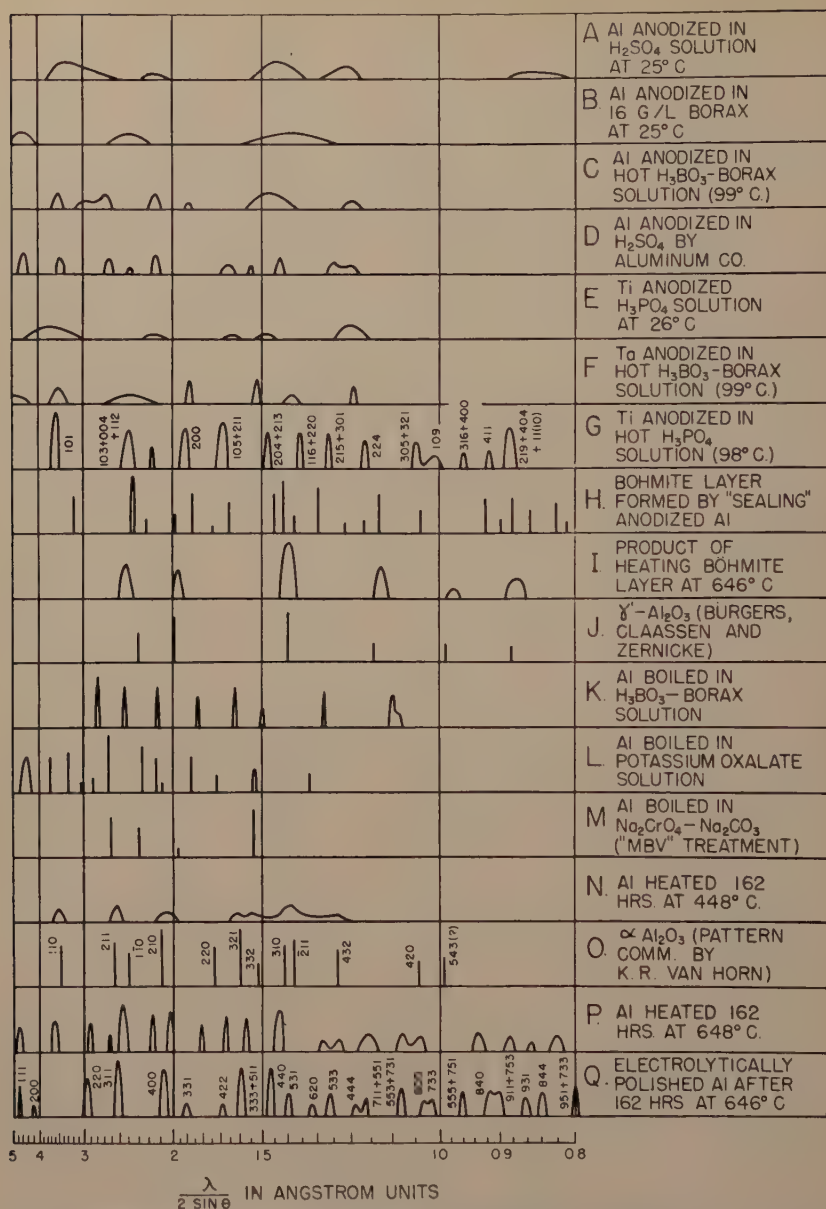


FIG. 1.—DIFFRACTION-PATTERN DIAGRAMS REPRESENTING POSITIONS, BREADTHS AND RELATIVE INTENSITIES OF RINGS IN PATTERNS.

Heights of curves should be understood to represent a comparison of intensities within a single diagram only.

in the diagrams are proportional to the corresponding distances between rings on the electron diffraction plates. The scale at the bottom of the figure gives value of $\frac{\lambda}{2 \sin \theta}$; for sharp rings these are equal to interplanar spacings in crystalline material. For amorphous material (having broad bands) there is not necessarily any important spacing in the material equal to the value of $\frac{\lambda}{2 \sin \theta}$ at the diffraction maximum.¹⁸⁻²⁰

Most of the diffraction patterns of anodic films consisted of a few broad, diffuse bands rather than the sharp rings ordinarily obtained from crystalline material. Typical of these is Fig. 2, obtained from an aluminum specimen anodized at room temperature in sulphuric acid solution. This diffraction pattern is represented schematically by the curves of Fig. 1-A. Anodic films formed at room temperature in $\frac{1}{2}$ normal solutions of other electrolytes, including phosphoric and oxalic acids, Na_3PO_4 , Na_2CO_3 , NaHCO_3 , borax, and ammonia, gave diffuse patterns of the same general appearance. Figs. 3 and 4, obtained from anodic films formed on aluminum at higher temperatures, show bands that are not as broad as those of Fig. 2. Fig. 4 (see also Fig. 1-C) does not agree with the sharp X-ray pattern obtained by Burgers, Claassen and Zernicke³ from a specimen similarly anodized (Fig. 1-J). Fig. 5 (see also Fig. 1-D), which shows a few sharp rings, is the pattern of an anodic film prepared through the cooperation of Dr. W. L. Fink at the Research Laboratories of the Aluminum Company of America, New Kensington, Pa. The relatively sharp rings in this pattern indicate that a crystalline material is present, possibly in addition to an amorphous material whose diffraction pattern consists of broad bands.

Anodic films on metals other than aluminum often had diffuse diffraction patterns, especially if formed under conditions in which the films were highly insulating. Tantalum anodically treated in borax solution and titanium anodized in phosphoric acid solution (Fig. 1-E) (both at room temperature), gave diffuse diffraction patterns like Fig. 2. Tantalum anodized in H_3BO_3 -borax solution at boiling temperature gave the pattern of Fig. 1-F, consisting of a few sharp rings and a few broad bands, neither of which coincided with the diffraction maxima obtained by Burgers, Claassen and Zernicke³ for a similarly treated specimen. The specimen of titanium anodized in boiling H_3PO_4 solution gave the pattern represented in Fig. 1-G, which agrees very well with the X-ray pattern of Burgers, Claassen and Zernicke for anodized titanium. These authors attribute their pattern to the anatase (tetragonal TiO_2) structure. The fifth and seventh rings of both the X-ray and electron diffraction patterns correspond to pairs of anatase rings (105 and 211, 116 and 220). The coincidence of each doublet for the anodic films suggests the axial ratio $\sqrt{6}$ (or 2.45) for the tetragonal lattice instead of the value 2.51 obtained

from Wyckoff's data for anatase.⁸ A calculated pattern using the axial ratio 2.45 agrees very well with observed spacings and intensities of the pattern of this anodic film. The modified tetragonal lattice has parameters $a = 3.81 \text{ \AA.}$ and $c = 9.35 \text{ \AA.}$, as compared with 3.78 \AA. and 9.50 \AA. for ordinary anatase. The third ring of Fig. 1*G* does not arise from the



FIGS. 2-5.—DIFFRACTION PATTERNS OF ALUMINUM.

Fig. 2. Anodized in 0.5 normal H_2SO_4 at 25°C. (See Fig. 1-A.)

Fig. 3. Anodized in 0.5 normal H_2SO_4 at 98°C.

Fig. 4. Anodized in H_3BO_3 -borax solution at 99°C. (See Fig. 1-C.)

Fig. 5. Anodized by the Aluminum Company of America in H_2SO_4 solution. (See Fig. 1-D.)

tetragonal lattice. It is sharper than the other rings and apparently belongs to a different substance. In the pattern of titanium anodized at room temperature a broad band appears at the position of this third ring.

When the broad-band pattern of Fig. 2 and other similar patterns had been obtained, it was deemed necessary to determine whether the diffuseness was due to the structure of the film material or to other causes.

Kirehner⁹ and others have pointed out that diffuse electron diffraction patterns may be obtained from surfaces that are smooth enough to give large refraction effects. To determine whether or not the broad band patterns were due to the surface finish, an aluminum specimen anodized in sulphuric acid solution was abraded lightly with grade 0000 emery



FIG. 6.—BÖHMITE LAYER PRODUCED BY "SEALING" ANODIZED ALUMINUM IN HOT WATER. (SEE FIG. 1-*H*.)

FIG. 7.—FACE-CENTERED CUBIC CRYSTALS FORMED ON ELECTROLYTICALLY POLISHED ALUMINUM BY HEATING AT 646°C. (SEE FIG. 1-*Q*.)

paper and electron diffraction patterns were taken before and after abrasion. The two patterns, each consisting of broad bands, were identical within the errors of measurement.

Another possible cause of diffuseness of the pattern is the charging-up of a film due to emission of secondary electrons during the electron diffraction exposure. The charge can become great when the film is a good insulator such as an anodic film, and can so seriously distort the

patterns as to make them appear diffuse. It was found that this distortion could be minimized by rotating the specimen during the exposure. The specimen was turned at 30 r.p.m. about an axis normal to the surface being investigated, and the electron beam struck this surface at a point one or two millimeters away from the axis. The charge then had an opportunity to leak away from each point of the surface during the part of the revolution in which the electron beam was striking the surface elsewhere. The use of this method gave sharp diffraction patterns when crystalline material was present, even with specimens that had a strong tendency toward charging up (e.g., Figs. 5 and 6), but the diffuse ring patterns were unchanged. It is concluded, therefore, that the diffuse rings are not due to electrostatic charging.

INTERPRETATION OF THE DIFFUSE PATTERNS

The diffraction pattern of Fig. 2 and patterns of several anodic films formed in other ways are diffuse enough to be similar to X-ray patterns of glass.¹⁰ This admits the possibility that the anodic films giving such patterns are amorphous, in the same sense that glass is amorphous. Another possible interpretation of the broad ring patterns is that they may arise from crystalline material of small grain size. According to the work of Scherrer¹¹ on the broadening of diffraction rings due to small grain size, the half-intensity width of the rings is given (for small glancing angles) by

$$B = 0.94 \frac{\lambda}{D}$$

where B is the ratio of the width of the ring to the distance from specimen to plate and D is the length of the edges of the crystals, which are considered cubic in shape. Taking the width of the rings to be 0.2 cm. (as it often measured) gives $B = 0.0049$. With $\lambda = 0.064 \text{ \AA.}$, this gives $D = 12 \text{ \AA.}$ * Since this size is less than twice the edge of the unit cell of cubic $\gamma\text{-Al}_2\text{O}_3$, it seems to the authors that there is little real difference between an amorphous material and a crystalline material of this grain size. With the anodic films formed at higher temperatures, however (Figs. 3 and 4), by the same reasoning a crystal size of 30 to 80 \AA. is obtained. In these cases it is perhaps most desirable to describe the film material as fine-grained crystalline.

It was thought that under high-temperature conditions there might be a transition of amorphous or microcrystalline anodic films to crystalline material of large grain size. Accordingly, several aluminum specimens anodized in $\frac{1}{2}$ normal H_2SO_4 solution were heated for 160 hr. at

* Because this method of grain-size estimation is subject to many kinds of errors the results can be taken as giving only the order of magnitude.

temperatures up to 650°C. These treatments failed to bring about any significant changes in the diffraction patterns of the films.

In the specimen anodically treated by the Aluminum Company of America there is undoubtedly some crystalline material present. Here differences in electrolytes or differences in the preparation techniques may account for the contrast between Fig. 5 (Fig. 1-D) and Fig. 2 (Fig. 1-A).

The disagreement between Fig. 4 (Fig. 1-C) and the corresponding X-ray pattern of Burgers, Claassen and Zernicke³ (Fig. 1-J) may be due to a difference between the structure near the surface of the anodic film (which determines the electron diffraction pattern) and the structure of the underlying film material. It may also be due to differences in the history of the films subsequent to anodic treatment, since Burgers, Claassen and Zernicke removed their film by dissolving the underlying aluminum, then washed the film material and dried it by heating at 80°C. The disagreement in the case of tantalum may be due to material other than tantalum which had been present on the electron diffraction specimen before anodic treatment. This material (possibly an oxide of tantalum) prevented the appearance of the diffraction pattern of the metal prior to the anodizing treatment.

IMMERSION TREATMENTS

In commercial practice, protective aluminum anodic films are made impermeable to stains either by a steam treatment or by a hot-water dip. Such treatments seal the pores of the anodic film by filling them with a softer material. Each aluminum specimen of Table 1 was immersed in boiling water for 30 min. After this treatment each specimen, without exception, gave the pattern of Fig. 6 (Fig. 1-H). This pattern has been identified as that of böhmite¹² or $\alpha\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$; it agrees with the pattern of Schmid and Wassermann¹ for a steam-treated anodic film, and agrees roughly with several of the aluminum hydroxide patterns given by Biltz, Lehrer and Meisel.¹³ Fig. 6 shows rings that are stronger in some parts than in others, which indicates a slight degree of preferred orientation of the böhmite crystals. Because the structure of böhmite has never been reported, it has not been possible to determine the nature of this preferred orientation.

An attempt was made to find the X-ray diffraction pattern of the böhmite layer by transmitting a beam of soft (Fe-K) X-rays through several thicknesses of aluminum foil that had been anodized in sulphuric acid until it was transparent, and then boiled in water for an hour. The X-ray showed only a faint pattern due to the residual aluminum, indicating that the böhmite layer was very thin in comparison with the rest of the anodic film. After a very light abrasion with grade 0000 emery paper a "sealed" anodic film no longer gave the pattern of böhmite; instead it gave a diffuse pattern. This again indicates that the layer is fairly thin.

However, it must not be concluded from this abrasion experiment that böhmite is formed only over the top surface of the anodic film. Undoubtedly it is formed throughout the minute pores that extend into the anodic layer. Abrasion would expose too little of this interstitial böhmite to be detectable.

Treatment of unanodized aluminum in boiling water produced a film giving the böhmite pattern. This identifies böhmite as a hot-water corrosion product of aluminum. Electron diffraction experiments showed that böhmite can be formed on both anodized and unanodized aluminum in water at temperatures of 80°C. and above, but not at 60°C. Immersion of anodized tantalum and titanium in boiling water did not produce an analogous crystalline material.

An aluminum specimen that had been anodized in sulphuric acid and "sealed" in hot water at the Aluminum Company laboratories gave a pattern that coincided with Fig. 6, although the rings were broader so that fewer of them appeared, and undoubtedly böhmite was present. After this specimen had been heated for 165 hr. at 646°C., it gave the pattern of Fig. 1-I, which is nearly identical with the X-ray pattern (γ' -Al₂O₃, Fig. 1-J) obtained by Burgers, Claassen and Zernicke³ from an anodic film that had been removed, washed and dried at 80°C. It was not determined in the present work whether or not such a treatment can produce γ' -Al₂O₃ from other anodic film material; but it seems possible that such a treatment could transform at least a portion of an amorphous film to a crystalline substance.

Immersion treatments are often used commercially for protection of unanodized aluminum against corrosion. In these processes aluminum is dipped in a boiling chemical solution, which forms a protective film. Some of the aluminum specimens were treated for 30 min. in boiling solutions of the following compositions: (1) a bath identical with that used for anodic treatment by the method of Burgers, Claassen and Zernicke,³ containing 100 grams boric acid and two grams borax per liter; (2) a bath patented by Newsome,¹⁴ containing 2.5 per cent potassium oxalate; (3) a similar bath with an addition (recommended in Newsome's patent) of 0.4 per cent sodium aluminate; and (4) a modified Bauer-Vogel (MBV) bath, similar to that widely used in Germany,¹⁵ containing 5 per cent sodium carbonate and 1.5 per cent sodium chromate.

All of the immersion treatments of aluminum produced definitely crystalline substances, giving sharp ring patterns in contrast to the usual case for anodic films. Immersion in Burgers, Claassen and Zernicke's solution produced a substance (Fig. 1-K) whose pattern could not be identified as due to an aluminum compound of known structure. An unsuccessful attempt was made with Hull-Davey charts to find the crystallographic system of this substance. Newsome's oxalate bath produced a film whose pattern (Fig. 1-L) is consistent with a hexagonal

lattice having $a = 5.26 \text{ \AA}$, $c = 14.88 \text{ \AA}$. The same bath with sodium aluminate added produced a böhmite film. The MBV bath produced a film whose diffraction ring radii were in the ratio $\sqrt{6}:\sqrt{8}:\sqrt{11}:\sqrt{18}$ (Fig. 1-*M*). Too few rings were present for any conclusion as to whether or not the film has a cubic structure. The rings would be consistent with a cubic structure having lattice parameter 6.50 \AA .

HEAT OXIDATION OF ALUMINUM

"Reflection" electron diffraction patterns of air-formed oxides on aluminum have not been previously reported. Accordingly, for a comparison of the diffraction patterns of anodic films with patterns of films formed by oxidizing aluminum in air, a group of aluminum specimens of 99.95 per cent purity was heated for 160 hr. at various temperatures up to 650°C . Before heating, the specimens were polished with fine alumina and each showed the diffraction pattern of metallic aluminum. Heating at temperatures below 300°C . produced only broadening and weakening of the aluminum rings, which would be expected if the aluminum surface were covered with a very thin layer of amorphous oxide.

Treatment of aluminum at temperatures between 300° and 450°C . produced patterns like that of Fig. 1-*N*. In these patterns the rings were faint and somewhat broadened so that their radii were difficult to measure. However, there is a surprising coincidence between observed maxima and those of $\alpha\text{-Al}_2\text{O}_3$ (Fig. 1-*O*).^{*} Despite this coincidence, it seems unlikely that $\alpha\text{-Al}_2\text{O}_3$ would be formed at such low temperatures, especially since other compounds appear at the higher temperatures. The pattern of the air-formed oxide that Steinheil¹⁷ has named $\epsilon\text{-Al}_2\text{O}_3$ was not found in any of these experiments.

After heating aluminum at temperatures from 550° to 650°C ., a variety of crystalline patterns (e.g., Fig. 1-*P*) was obtained, each apparently due to two or more crystalline substances. One of these substances occurred alone on a specimen that had been polished electrolytically by Jacquet's method¹⁶ and heated 162 hr. at 646°C . This specimen gave a pattern (Fig. 1-*Q*) that corresponds to a face-centered cubic lattice with parameter $a = 8.30 \text{ \AA}$. The positions of the relatively intense parts of several of the rings indicate that the crystals have a slight tendency to lie with their 111 planes parallel to the surface of the specimen. The pattern is somewhat similar to that of $\gamma\text{-Al}_2\text{O}_3$, but there are distinct differences both in the lattice constant and in the indices of rings that are present. The lattice constant is in the range of the spinels, although it seems probable that the material is nearly pure aluminum oxide. Oxidation products of thin aluminum foil produced by evaporation never gave pat-

^{*} Drawn from X-ray measurements given to the authors in a private communication through the courtesy of Dr. Kent R. Van Horn of the Aluminum Company of America.

terns similar to those mentioned above. By treatment of foil at temperatures greater than 500°C. γ - Al_2O_3 was always obtained.

DISCUSSION OF RESULTS

It should be pointed out that the results obtained by electron diffraction on anodic films can be strictly said to apply only to the structure within about 10^{-6} cm. of the surface. To investigate material below this depth by electron diffraction it would be necessary to abrade or etch away successive strata of the films. An alternative would be to remove the films entirely and use X-ray diffraction or chemical analysis, but these methods would not detect thin surface layers which electron diffraction experiments might reveal. Comparison of the present work with that of Burgers, Claassen and Zernicke³ indicates that in some cases the surface structure of an anodic film may be quite different from that of the underlying material.

When sharp diffraction patterns are obtained it is possible to identify the crystalline material from which they have come, first by comparing the unknown pattern with the available diffraction patterns of known crystalline substances, and second, if this fails, by synthesizing compounds and obtaining their diffraction patterns until the unknown is duplicated. Thus it is possible (though often not easy) to find the chemical composition of a specimen if its diffraction pattern is sharp. In the case of amorphous materials it is not possible to determine the chemical composition by a diffraction pattern alone, since two chemically different amorphous materials may have identical or nearly identical diffraction patterns.* In the case of anodic films on aluminum the chemical composition is uncertain with regard to water content. The diffuse diffraction patterns of anodic films, then, cannot be interpreted fully without further experimental results.

The crystalline patterns given here have been compared with all the readily available diffraction data on compounds with which they might be identical. For the compounds not identified in this way, the second step (synthesis of compounds and investigation of their diffraction patterns) has not been taken because of lack of time.

CONCLUSIONS

From the fact that aluminum anodized at room temperature usually gave diffuse patterns, it is inferred that anodic films formed on aluminum in a wide variety of electrolytes at ordinary temperatures are amorphous. Anodic treatment in solutions at higher temperatures tends to produce anodic films having less random structure, which may possibly be

* There are imaginable cases in which crystalline substances of different chemical composition might give identical diffraction patterns. Practically, this does not occur except for closely similar substances (e.g., the pair tantalum and columbium in the metallic state).

described as crystalline with very small grain size. Heating the anodic film on aluminum at temperatures up to 650°C. does not appreciably change its structure, although crystalline oxidation products are formed on unanodized aluminum at temperatures above about 300°C. In this respect the anodic film is different from the ordinary air-formed oxide film on aluminum, since the latter is probably transformed at these temperatures to crystalline substances.

Under certain conditions anodic films formed on tantalum and titanium are at least partly crystalline, and under other conditions they are probably amorphous.

Immersion of anodized or unanodized aluminum in water at temperatures above 80°C. produces a thin layer of böhmite ($\alpha\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$). A film produced in this way is transformed to $\gamma'\text{-Al}_2\text{O}_3$ at temperatures around 650°C. Immersion of metallic aluminum in boiling chemical solutions gives definitely crystalline films, in contrast to the usual results with anodic treatment.

ACKNOWLEDGMENT

The authors wish to thank Prof. F. C. Blake, of Ohio State University, and Dr. H. W. Russell, of Battelle Memorial Institute, under whose joint supervision the investigation of the problem was carried out. The authors also wish to thank Dr. W. L. Fink, of the Aluminum Company of America, for his cooperation in discussing the problem and in supplying specimens of aluminum.

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Determination of Orientations by Etch Pits

By CHARLES S. BARRETT,* MEMBER, AND L. H. LEVENSON,† JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1940)

THE orientation of metal crystals and grains, both large and small, can be determined conveniently and accurately without the use of X-ray apparatus. This seems to be appreciated by so few metallurgists that it may be useful to explain in detail the method we have found most satisfactory in the laboratory—the reflection of light from crystallographic etch pits. This note includes a description of a suitable inexpensive instrument and instructions for etching various metals and for plotting the data. As the stereographic projection is used to facilitate handling the data, this note may be considered as an appendix to an earlier review of the metallurgical uses of the stereographic projection.¹

Various methods involving etch pits have been used by other investigators. Bridgman's method² consists of attaching the specimen to a sphere (a transparent sphere is convenient⁴), holding it at arm's length, and marking a spot on it when it has been turned so that the etch pits reflect light into the eye of the observer from a lamp standing behind him. It has an accuracy of about 2° and is extremely rapid. A greater accuracy can be obtained by having the reflected light fall on a screen, as has been done by Czocharlski,⁵ Chalmers,⁶ and Schubnikov.⁷ All of these methods have been intended for undeformed single crystals. Tammann and his coworkers^{3,8} developed a method for estimating the number of grains in a polycrystalline aggregate having orientations in a given region of the stereographic triangle and thus obtained statistical information about deformation and recrystallization textures. While the method has had some use in recent years,⁹ it is not applicable to the majority of problems in physical metallurgy. Smith and Mehl¹⁰ determined orientations by plotting the directions of the sides of individual etch pits on a stereographic projection. The accuracy is limited to about 3° and the method requires careful polishing and high magnification.

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¹ References are at the end of the paper.

The most useful methods involve the measurement of the angles between the etch-pit faces in a goniometer, yet these seem to have received the least attention. Weerts¹¹ has given a lengthy discussion of a technique using a three-circle goniometer and polarized light. A less elaborate method, which gives an accuracy that is sufficient for the great majority of investigations, consists simply of measuring the orientations of the etch-pit faces on a two-circle optical goniometer. While this method has been briefly mentioned in notes by McKeehan^{12,12a} and by Potter and Sucksmith,¹³ with a few exceptions it has remained almost unused among metallurgists in spite of the fact that it is the equal of X-ray methods in many cases, having an accuracy of $\frac{1}{2}^\circ$ or 1° , and for certain problems it is definitely superior to them.

The difficulties usually encountered in methods of this type are in getting satisfactory etch pits, in eliminating multiple reflections from two or more faces of the pits, in distinguishing the etch-pit reflections from the irregularly scattered light, and in reflecting from etched planes lying nearly perpendicular to the surface of the specimen. With the apparatus and technique described in this paper, these difficulties are readily overcome. The method has been in nearly constant use for a year in this laboratory with such success that it is frequently chosen in preference to X-ray methods. It operates satisfactorily with grains as small as 0.1-mm. diameter and has been used with cold-worked and annealed grains and single crystals.^{14,15}

AN INEXPENSIVE GONIOMETER

An inexpensive two-circle goniometer may be constructed for this work from an old surveyor's transit (Fig. 1). It consists of the horizontal circle of the transit *H*; a vertical circle *V* (formerly the compass circle of the transit), mounted on the rotating cover of the horizontal circle; a shaft through the vertical circle for supporting the specimen *S*; a light and collimator *C*; and the transit telescope *T*, all mounted on a base plate. The specimen *S* is mounted with plasticene on the face plate *F*, on which are engraved concentric circles for aid in centering. (For wires or rods the face plate may be replaced by a small chuck.) The specimen surface is made to lie on the axis of the horizontal circle *H* by rotating the threaded shaft of the face plate through the hub of the vertical circle. When this adjustment is complete, the shaft is fixed in position by means of a lock nut, which causes the vertical circle to rotate with the specimen. The specimen is illuminated by parallel light from the collimator *C*, which contains a 6-volt lamp and lens, and is observed in the transit telescope *T*, which has cross hairs. For ordinary measurements of single crystals or large grains, a magnification of two or three times is used in the telescope. Higher magnifications may be obtained

by inserting additional lenses in the objective tube without altering the other adjustments of the goniometer.

The grain to be measured is placed at the intersection of the vertical and horizontal axes of the instrument, and the axes of the telescope and collimator are made to intersect at this point. The axes of the collimator and telescope lie in a vertical plane and make equal angles of about 10° with the horizontal; with this arrangement, light that is multireflected from the three faces of an etch pit of cubic shape is returned in the incident direction and not seen in the telescope. With this instrument the positions of maximum reflection can be observed even when the specimen

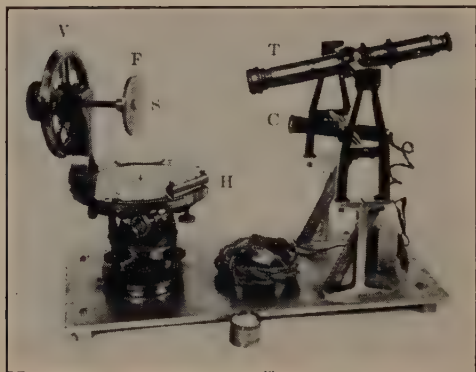


FIG. 1.—OPTICAL GONIOMETER.

Specimen *S* is mounted on face plate *F*, which turns with vertical circle *V*. *V* is mounted on rotating cover of horizontal circle *H*. Axes of telescope *T* and collimating tube *C* intersect at *S*.

surface is within 5° of parallelism with the viewing direction; i.e., from etch-pit faces that lie almost perpendicular to the surface. A darkened room is best for the work.

ETCHING TECHNIQUE

A large number of etchants for developing crystallographic etch pits have been described in the literature, but we have so frequently been disappointed in the results they yield that we have worked out an independent list that appears to be entirely satisfactory. In the footnote to Table 1, reference is made to the etchants recommended by other investigators.

An ideal etchant would be one that develops etch pits or facets with plane faces accurately parallel to crystallographic planes of low index. The etched metal specimen would then appear intensely bright when the normals to these planes bisected the angle between telescope and collimator, and perfectly black in all other positions. Actually, however, the etch-pit faces are always more or less rounded, causing the intensity of

TABLE 1.—*Directions for Etching*

Metal	Purity, Per Cent	Etchant ^a	Etch- ing Time, Min.	Planes Developed	Remarks
Aluminum....	99.95	9 parts HCl 3 parts HNO ₃ 2 parts HF 5 parts H ₂ O	2	{100}	Use large quantity of etchant with respect to surface of specimen and avoid heating of etchant.
α -iron.....	H ₂ purified de- carburized mild steel	1 part HNO ₃ 4 parts H ₂ O	4	{100}	Avoid heating, as above; wipe during etching.
Copper.....	OFHC	1 part HCl 1 part H ₂ O; mixture saturated with FeCl ₃ ·6H ₂ O	10	{100}	
Brass.....	Cartridge Brass 70-30	1 part etch for Cu 1 part H ₂ O	20	{100} and {111}	Agitate etchant at 2-min. intervals.
Lead.....	99.9	3 parts H ₂ O ₂ 2 parts glacial acetic acid 2 parts H ₂ O	10	{100}	
Tin.....	99.991	1 part etch for Cu 1 part H ₂ O	10	{100} and {110}	Wipe off at 2-min. inter- vals.
Tungsten....		100 parts saturated K ₃ Fe(CN) ₆ 5 parts saturated KOH 95 parts H ₂ O	15	{110}	Agitate etchant at 2-min. intervals. Composition of etch is critical.
Zinc.....	99.99	7 parts saturated CuCl ₂ ·2H ₂ O 3 parts HCl 90 parts H ₂ O	3	{101}, 1 having m a n y values	Wipe off deposited copper at 30-sec. intervals. Maximum reflections lie in three planes intersect- ing at pole of basal plane. Hexagonal axes lie 90° from the intersection and midway between these planes.

^a For other etchants, which have been used by various investigators, see the following references listed at the end of the paper. 22, 13, Al; 10, 13, 3, Fe; 18, 19, 3, 20, 25, Cu; 4, Pb; 6, 2, 12a, Sn; 3, Zn; 24, Ag; 3, 23, Au; 3, 13, Ni; 2, 21, W.

the reflected light gradually to build up to and drop off from a maximum as the reflecting plane approaches and recedes from the reflecting position. For the same metal and etchant, the position and sharpness of the maximum vary with the etching time and the temperature of the etchant. When the maxima are sharp enough to be reproducible within $\frac{1}{2}^\circ$, their positions usually coincide with the crystallographic poles, but sometimes they tend to fall a degree or two away from true crystallographic poles. For example, maximum reflections from cubic etch pits are often 88° or 89° , rather than 90° , apart. Since only two poles are necessary to deter-

mine the orientation, and three can usually be measured, the observed poles can be corrected by moving them a minimum amount to make them mutually perpendicular. Occasionally a few large noncrystallographic pits are developed and may be readily recognized as such, since they have no definite maximum.

In Table 1, directions are given for etching various metals for orientation work. The etching times are for etchants at room temperature and for strain-free metals of the purity indicated. For metals whose purity is not too far from those in the table, suitable variation of the etching time will produce desirable etch pits; for cold-worked metals, the etching time must usually be reduced. The degree of polish of the surface has very little effect, and No. 00 emery paper has been found to be sufficiently fine. When the angles between the observed reflections agree with actual angles between crystal planes, full confidence can be placed in the determination. X-ray diffraction tests have always agreed with the optical data in our tests to 1° or better.

METHOD OF PLOTTING

The readings on the two circles of the goniometer corresponding to a reflection maximum (a cube pole, in this discussion) can be plotted directly as a point on a stereographic projection. A Wulff net* 15 to 20 cm. in diameter gives all the accuracy required for the most problems—about $\frac{1}{2}^\circ$. The data are plotted on tracing paper fastened to the net by a pin at the center of the net, the paper being left free to turn about the pin.

Transferring data from the goniometer to the projection is direct and simple, for readings on the horizontal circle of the goniometer correspond to radial distances from the center of the projection and readings on the vertical circle correspond to azimuthal positions around the center, if one makes the plane of the projection parallel to the surface of the specimen.

Let us illustrate with an example in which it is desired to find the orientation of the cube poles within a portion of a grain in a rolled specimen with respect to the rolling direction and the normal to the rolling plane. A small mirror is first placed on the face plate *F*, Fig. 1, the instrument adjusted to reflect the light into the telescope, and the horizontal circle turned so as to read zero at this setting. The specimen is then placed on the face plate and adjusted with plasticene until its surface lies at the intersection of the axes of the instrument and parallel to the face plate, and the rolling direction is made to lie vertically when the vertical circle reads zero. Assume that to bring the specimen into a posi-

* E. Leitz, New York City, sells a Wulff net both with and without a revolving base. Stereographic nets with 2° graduations are reproduced by D. Jerome Fisher: Problem of Two Tilts and the Stereographic Projection, *Bull. Amer. Assn. Petr. Geol.* (1938) **22**, 1261.

tion of maximum reflection requires a 30° clockwise (looking through the telescope) rotation of the vertical circle and a 40° clockwise (looking down) rotation of the horizontal circle. The pole of this reflecting plane is plotted by rotating the tracing paper 30° clockwise about the center of the net from the position in which RD is at the north pole, and marking a point 40° to the right of the center on the equatorial line of the net. The pole A in the projection of Fig. 2 is plotted thus, with the rolling direction indicated on the boundary circle at RD . The same plane can also be brought into reflecting position by a 150° counterclockwise rotation of the vertical circle and a 40° counterclockwise rotation of the horizontal circle. Thus, for each of the faces of an etch pit there are two settings for maximum reflected intensity 180° apart on the vertical circle and symmetrical with respect to the zero position of the horizontal circle. The closeness with which these two plotted points agree on the projection is a check on the alignment of the apparatus and the reliability of the readings. The other two cube poles, B and C , are found and plotted similarly, and, as shown in Fig. 2, lie 90° apart on a great circle 90° from A . The third pole may at once be plotted 90° from the other two, but it is better to use its experimentally observed position as an internal check on the accuracy of the orientation determination.

The surface normal is at the center of projection when the plotting is done as described above, and its angular distances from the three cube poles can be read from the projection or directly from the horizontal circle. The angles between the plotted poles and the rolling direction can be found by rotating the plot until the rolling direction lies at the north pole of the net and reading the colatitudes of the poles.

APPLICATION TO DEFORMED METALS

The optical goniometer has especial value in the study of lattice orientations in deformed grains and single crystals where X-ray work becomes extremely difficult, if not impossible. Lattice orientations of deformation bands a few tenths of a millimeter wide have been measured in severely deformed aluminum.¹⁵ In general, with either single crystals

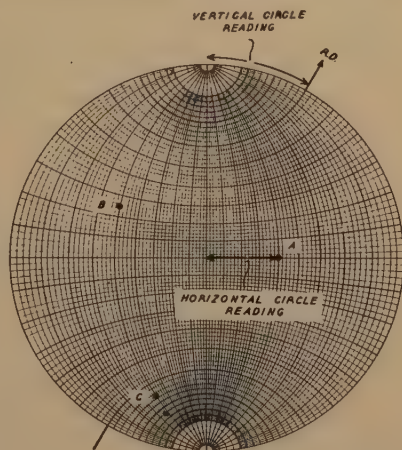


FIG. 2.—GONIOMETER READINGS FOR A ROLLED CUBIC CRYSTAL PLOTTED ON A STEREOGRAPHIC PROJECTION.

Points A , B and C correspond to cube poles of the crystal and are mutually perpendicular. Surface normal is at center of projection; rolling direction, indicated by $R.D.$, is on periphery.

or grains of a polycrystalline aggregate, the orientation after deformation varies considerably and in an irregular manner over the grain. In determining the range of orientation of a grain, it is divided into a number of areas, from three to ten or more, depending on the size of the grain, the total variation, and the accuracy required, and the orientation of each area is measured separately.¹⁵ The envelope of the points then bounds the range of orientation, and the "center of gravity" of the points is the mean orientation. The orientation of each area may be separately transferred to a standard projection, and the grouping of points on the final projection gives a pole figure of the preferred orientations present. This technique has been used to prepare pole figures of polycrystalline specimens, both in cold-worked and recrystallized states,^{15,26} when the individual grains were a few millimeters in diameter. For this purpose it has the advantage of being quantitative (this is difficult with X-rays), but it does not, of course, detect the fragments of microscopic or sub-microscopic size that can be registered by X-rays.

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DISCUSSION

(W. L. Fink presiding)

L. P. TARASOV,* Schenectady, N. Y.—What is the factor that sets at 0.1 mm. the lower limit of grain size that can be studied? Is it the practical difficulty of handling the goniometer and telescope in studying very small grains, or is there any trouble in etching these small grains in a suitable manner?

It may be possible to measure the orientations on a statistical basis by substituting a photocell for the observer's eye and scanning the specimen for a large number of different angular positions. Provided the irregularly scattered light does not interfere too much, the integrated light output for each position would furnish a small area on the pole figure having the proper intensity.

C. S. SMITH,† Waterbury, Conn.—Do multiple internal reflections from two or more surfaces of the same etch pit complicate the interpretation of the results?

C. S. BARRETT (author's reply).—For cubic etch pits, a ray that is reflected from all three faces is returned in the incident direction regardless of the order in which it strikes the faces. Such rays are reflected back into the collimator and are not seen in the telescope, which is on the opposite side of the horizontal axis in the instrument of Fig. 1. Rays that are reflected from exactly two faces are returned in three different directions; the intensity of such doubly reflected rays in any given direction is small and cannot be distinguished from the irregularly scattered background illumination. We have found that well developed etch pits give exceedingly sharp maxima, whose angular distance apart checks that of the corresponding crystallographic planes. This is true not only for cubic pits but also for octahedral pits (in brass) and dodecahedral pits (in tungsten).

The minimum grain diameter (0.1 mm.) mentioned in the paper refers to those we have actually measured, and is not an inherent lower limit of the method. For smaller grain sizes the etches given might have to be modified to produce finer pits. In measuring small grains not only must the magnification of the telescope be increased,

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but also the alignment of the instrument must be good enough to keep the grain being measured on the intersection of the cross hairs for all settings of the vertical and horizontal circles.

The use of a photocell for the statistical measurement of the orientations of fine grains, as proposed by Dr. Tarasov, would require some important corrections, because, for any individual grain, the intensity of each maximum depends on the angle between the face of the etch pit and the specimen surface, the relation being of a cosine type. With a photocell pole figure of an aggregate known to be perfectly randomly oriented, it should be possible, however, to correct the intensities in an observed pole figure so as to give a true pole figure. A more immediate use of the photocell might be in the precise setting of maxima from single crystals.

The Process of Precipitation from Solid Solution, I— A Crystallographic Mechanism for the Aluminum-copper Alloys

BY CARL H. SAMANS,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

IN their recent complete review of the subject of age-hardening,¹ R. F. Mehl and L. K. Jetter classify the main types of precipitation-hardening alloys under two headings, depending upon the nature of the precipitate and the character of the precipitation. In the alloys falling under the first heading, which display "continuous precipitation" and are typified by the aluminum-copper alloys, "precipitation seems to occur without much regard to grain boundaries and apparently at much the same rate at every point," although an acceleration in regions plastically deformed has definitely been established.² In the second type of alloys the precipitation is "discontinuous," as in the copper-silver system for example, and "seems to start in restricted regions, primarily those contiguous with the grain boundaries, and to spread inward in an advancing wave." The reasons for the occurrence of these two greatly different types of precipitation are unknown, as are those for many other reactions that take place in the solid state.

In the present paper only the first or "continuous" type of precipitation will be dealt with, for which a complete crystallographic mechanism has been worked out for the process of precipitation from a supersaturated solid solution of copper in aluminum. Based upon this mechanism, an explanation of the various property changes found experimentally will be developed in the second paper of this series. In later papers "discontinuous precipitation" in copper-silver alloys will be explained, and an effort will be made to rationalize the two processes and types of precipitation.

CRYSTALLOGRAPHY OF THE PRECIPITATION PROCESS

Through the extensive investigation by R. F. Mehl, C. S. Barrett and F. N. Rhines³ on the Widmanstätten structure in aluminum-rich copper

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¹ References are at the end of the paper.

alloys, the equilibrium precipitate, θ -CuAl₂, is indicated as taking the form of plates parallel to the {100} planes of the solid solution lattice. However, subsequent work, chiefly that of G. Wassermann and J. Weerts,⁴ whose data have been amply confirmed by others, has shown that the precipitating phase is not the equilibrium one, but, instead, a tetragonal phase with $a_0 = 8.2$ and $c_0 = 11.6$ Å. More recently G. D. Preston⁵ has been able to establish more accurately the parameters of this phase, which we shall designate as θ' -CuAl₂. He has shown it to be of the calcium fluoride type, but slightly tetragonal with $a_0 = 5.71$ Å. and $C = 1.015$. That these data are in concordance with those of Wassermann and Weerts was first pointed out by W. L. Fink and D. W. Smith.⁶ It should be noted, however, that the relative orientations between the solid solution and the θ' -CuAl₂, found by Preston, are not in agreement with those indicated as most probable for θ -CuAl₂ by Mehl, Barrett and Rhines, although the latter authors did suggest them as an alternative possibility.

The so-called "Widmanstätten mechanism" for solid-solid precipitation reactions is essentially of the interface type, even though in their review Mehl and Jetter do modify this concept to a certain extent by the statement that "the atom movements by which the matrix lattice becomes the precipitate lattice may often be represented as a series of shearing operations, sometimes simple and sometimes complicated." Inasmuch as a true interface reaction is possible, fundamentally, only when there is complete incompatibility of the two phases, it would seem to be a prerequisite of these transformations that they be explainable in nearly every case by a series of shearing operations, and that a "block" or "zone" transformation consequently be the true one. The fact that complete incompatibility—i.e., insolubility—is seldom if ever found in metallic systems is, of course, well known today. The results of the Widmanstätten studies therefore give at most the relationship between the initial and final states of the process, which, valuable clues though they be, leave unexplained the precipitation mechanism.

The initial stages of the precipitation process have been thoroughly considered by W. L. Fink and D. W. Smith⁷ in their discussion of the theory. They pointed out that even in a statistically uniform solid solution there will be a definite probability of occurrence of groups of various sizes which will contain any given number of copper atoms. Furthermore, by use of the Poisson Distribution Equation, they were able to compute this probability.

While it is true that the Poisson equation tells nothing of the effect of temperature upon the distribution nor of the probable life period of an aggregate of atoms, the effect of temperature must be rather small if the quench from the solution treatment is rapid, since it acts chiefly through its effect on the diffusion rates of the atoms involved. Consequently it is

felt that Poisson's equation gives a sufficiently good approximation of the distribution actually occurring in the aluminum-copper solid solutions, at least in the temperature range of age-hardening for these alloys.

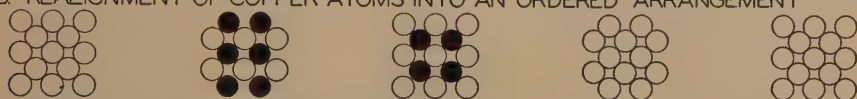
The nuclei of the more stable θ' -CuAl₂ phase, therefore, would be expected to form by the transformation of these atomic groups. This transformation is postulated as taking place in four stages:

1. The formation of the atomic groups already described, which contain, by pure chance, the correct number of copper atoms and are of sufficient size to be stable at the temperature of precipitation. In these groups, since at the solution temperature they are in a constant state of

A. AN ATOMIC GROUP IN THE SOLID SOLUTION



B. REALIGNMENT OF COPPER ATOMS INTO AN ORDERED ARRANGEMENT



C. REARRANGEMENT INTO A NUCLEUS OF θ' -CuAl₂

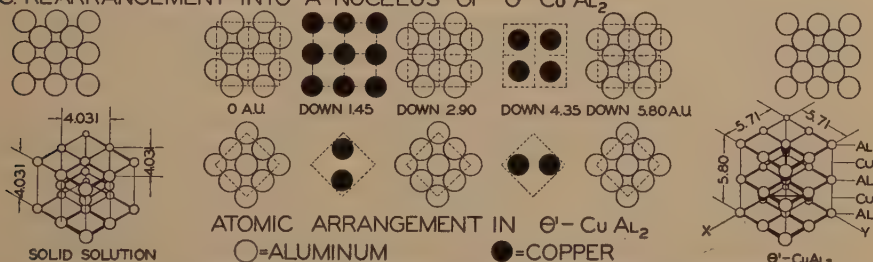


FIG. 1.—ATOMIC POSITIONS FOR VARIOUS STAGES IN PROCESS OF PRECIPITATION OF θ' -CuAl₂ OUT OF A SUPERSATURATED ALUMINUM-COPPER SOLID SOLUTION.

The groups of atoms represent successive planes parallel to (001). The plane designated 0 A.U. is the upper one of a set, in each case. Succeeding planes then are located a certain distance below this top plane; e.g., "Down 4.35" means 4.35 Å. below the top plane.

flux, the copper atoms would be expected to have a random arrangement as shown in Fig. 1A.

2. Realignment of the atomic groups to give the more symmetrical "ordered" arrangement of copper atoms shown in Fig. 1B, but still retaining the symmetry and atomic positions of the face-centered cubic solid solution lattice.

3. Rearrangement of the atoms to form the θ' -CuAl₂ nucleus as shown in Fig. 1C. This is postulated as consisting of a change in position of the copper atoms from their former substitutional locations to new positions, which are interstitial between the former cube planes of the solid solution. This, naturally: (a) forces these planes farther apart; (b) produces a shear of one plane of atoms so that three successive cube planes

of the solid solution become identical in position as well as in arrangement; and (c) forms "holes" in the (001) planes where the copper atoms were formerly located but which now must be filled by aluminum atoms diffusing in from outside. Even after this rearrangement the nucleus will probably not as yet have the characteristics of the θ' -CuAl₂ phase, because of the restraining forces acting between it and the solid solution matrix. Likewise, because of these same forces, and the relatively low atomic mobility at the aging temperatures, the matrix might be unable to change its dimensions appreciably as precipitation proceeds.

4. Growth of the θ' -CuAl₂ plates until an interface is produced between them and the solid solution lattice. During this growth there is a mutual distortion of the two lattices, which increases until it produces an actual rupture (i.e., interface), allowing both the solid solution and the precipitate to assume their true characteristics.

DEFENSE OF SUGGESTED PRECIPITATE MECHANISM

The changes occurring during the precipitation process have recently been studied by means of improved X-ray techniques by G. D. Preston^{5,8,9} and by A. Guinier¹⁰⁻¹³ and his co-workers. The works of these authors are in general agreement and their results may be summarized as follows:

Within the solid solution lattice, and parallel to the {100} planes of it, "there exists a series of small parallel plane elements, dispersed at random, and composed of atoms different from those of the main lattice." These planes vary in extent between about 50 Å. at 25°C., and 150 to 200 Å. (initially) at 100° to 200°C. Guinier assumed that they were composed of copper atoms without making any hypothesis about the disposition of the atoms within the groups; and he estimated their thickness to be, on the average, 4 Å. (i.e., two atomic layers). Preston's estimate of thickness was two or three planes of atoms, and that of extent about the same as Guinier suggested. He also noted that after the θ' -CuAl₂ had been formed, the two crystals, although structurally different, "form one diffracting unit and the plane of union is (001)."

These data, therefore, give us three definite facts about the precipitation process: (1) the "disturbance" incident to precipitation takes place on cube planes of the original solid solution; (2) the thickness of the "disturbed" zone is about two or three atomic layers; and (3) in the precipitated θ' -CuAl₂ particle the (001) plane is parallel to an {001} plane of the solid solution and the [110] direction is parallel to an $\langle 100 \rangle$ direction in the solid solution.

Regarding now the four stages in the proposed precipitation mechanism, there should be little argument concerning the first one. The

possibility of occurrence, in the statistically uniform solid solution, of enriched and impoverished areas that form and disintegrate at a rate dependent on temperature seems quite logical, as does also the probability that the copper atoms in the groups are randomly distributed.

The second stage, realignment to an ordered arrangement, is more open to question. In view of the fact that in both the more stable θ' and θ - CuAl_2 structures the copper atoms never attain positions of closest approach, Guinier's assumption that his "planes" are composed of copper atoms alone does not seem to be entirely justified. The arrangement postulated here is the most concentrated required to supply all the copper atoms needed for the more stable compounds, and although it too gives planes that are composed entirely of copper atoms, they are of very limited extent since they lie perpendicular to the flat surface of the plate.

Mehl and Jetter's suggestion regarding the third stage differs considerably from that proposed here. Their concept ("The lattice of θ' may be considered as formed from the matrix by simple compression along the c -axis . . . with the simultaneous loss of several atoms . . . though this transformation can alternatively be expressed in terms of simple shearing operations"), while it sounds quite simple cannot be so because it is necessary to remove several aluminum atoms (i.e., four for each unit cell of θ' - CuAl_2 formed) from the transforming region. Furthermore, since this process of nuclei formation must be a diffusionless one, any number of successive simple shearing operations would be unable to account for the volume change. It is a well-known fact that simple shear is one of the two principal ways of producing deformation without a change in volume. Explanations of the process can be made using simple shears and contraction simultaneously or successively but the same two inherent objections to them will always arise: (1) Why should the first shear occur? (2) How are the excess aluminum atoms eliminated? In the mechanism suggested here both of these are overcome by the movement of copper atoms into interstitial positions. Firstly, only certain interstitial positions (i.e., those for which each copper atom will have two aluminum atoms for nearest neighbors) are possible, so that the planes occupied by copper atoms can attain only the required density of population. Secondly, from the geometry of the face-centered cubic structure, the movement of the copper atoms to the interstitial positions would automatically give the "push" necessary to start the shear required of the single plane in the solid solution lattice. Then, as the copper atoms are removed, substitutional positions are left vacant, and these can be filled by simple diffusion of aluminum atoms from outside the disturbed zone or from elsewhere in it. This is in conformity with certain phases of the Wagner-Schottky theory of diffusion by lattice imperfections.¹⁴ Also, it would be the process naturally expected since the expansion incident to the copper atoms

taking up their interstitial positions would tend to compress the surrounding aluminum atoms, and their diffusion into the vacancies would tend partly to relieve this compression.

It should be quite evident that the copper atoms, before changing position, would be obliged to obtain energy enough to surmount the potential barrier that tends to keep them in the substitutional position. Such a barrier would exist regardless of the net energy interchange of the process, which is probably exothermic. Consequently the atomic group cannot rearrange instantaneously as required by the theory of Fink and Smith⁷ or even "more or less at once" as suggested by M. L. Gayler,¹⁵ but must wait until one or more parts of it secure sufficient energy to start. The transformation probably would then spread out from this center at a more or less regular rate because of the net energy released by the process.

The fact that the equilibrium phase, θ -CuAl₂, is found to contain more aluminum than required for the stoichiometrical compound would be explainable in either or both of two ways: (1) aluminum, instead of copper, atoms are occasionally moved into interstitial locations, or (2) interstitial vacancies are occasionally formed because of an insufficient number of copper atoms to fill a plate completely.

The fourth stage, growth of the θ' -CuAl₂ plates, is introduced for definite reasons. Previous theories such as that of Gayler,¹⁵ which postulated growth before precipitation, have met with serious objection because they require that the copper atoms in the solid solution diffuse to regions in the same solid solution that are already enriched in copper. This "uphill" diffusion is anomalous and has never been found elsewhere. The present hypothesis, by forming nuclei directly from the groups, eliminates this possibility because their copper atoms are no longer in the solid solution when diffusion becomes effective. Furthermore, Guinier¹³ was able, at temperatures of 150°C. and higher, to detect the presence of the "oriented tetragonal" θ' -CuAl₂ phase before maximum hardness had been attained. Since, as will be discussed in Part II, a true interface probably does not appear between the solid solution and the precipitate until it has reached a size commensurate with maximum hardness, this general explanation of growth after the formation of θ' -CuAl₂ seems most satisfactory.

TRANSFORMATION OF θ' -CuAl₂ TO θ -CuAl₂

Inasmuch as the work of Preston has established the three essential points that (1) the metastable and the stable forms have the same composition, (2) their unit cells contain the same number of atoms, and (3) their orientation with reference to the solid solution matrix is similar at least with reference to the plane of contact, it seems logical to assume that the transformation from one to the other is essentially a process of

redistribution and readjustment to give an arrangement of lower energy. Everyone seems now agreed that this transformation does not take place until well after maximum hardness has been attained, and until the θ' -CuAl₂ particles have established their separate identities. It is true that Wassermann¹⁶ postulates some formation of θ -CuAl₂ at 300°C. right from the start of aging and that, at the same temperature, Guinier was able to detect it after 1 hr., but this was also well after the attainment of maximum hardening, and it is extremely doubtful that θ -CuAl₂ is ever found in appreciable amounts while the hardness is still increasing. At 200°C., for example, Guinier could not detect it even after 41 days of aging, and Fink and Smith¹⁷ found no appreciable change in the amount of the θ' phase after aging for as long a time as 42 days, although Wassermann¹⁶ did find it after 70 days.

Concerning the mechanism of the transformation, Mehl and Jetter¹ say: "But the transformation of θ' to θ requires lattice movements of unusual complexity, and doubtless requires high activation energy for its accomplishment, and occurs therefore at a slow rate." Other than this nothing specific was offered.

Let us examine first the parameters of the two phases. As previously mentioned, those of θ' -CuAl₂ have been shown to be $a_0 = 5.71$ and $c_0 = 5.80$ Å. the atoms being arranged in a slightly tetragonal modification of the CaF₂ type structure. The structure of θ -CuAl₂ has been determined most recently by Bradley and Jones¹⁸ to be tetragonal with $a_0 = 6.054$; $c_0 = 4.864$ with the coordinates of the copper atoms:

$$\begin{array}{ll} \frac{1}{2}, 0, \frac{1}{4} & 0, \frac{1}{2}, \frac{3}{4} \\ 0, \frac{1}{2}, \frac{1}{4} & \frac{1}{2}, 0, \frac{3}{4} \end{array}$$

and those of the aluminum atoms:

$$\begin{array}{ll} u, u, 0 & \bar{u}, \bar{u}, 0 \\ u, \bar{u}, \frac{1}{2} & \bar{u}, u, \frac{1}{2} \\ (u + \frac{1}{2}), (u + \frac{1}{2}), \frac{1}{2} & (\frac{1}{2} - u), (\frac{1}{2} - u), \frac{1}{2} \\ (u + \frac{1}{2}), (\frac{1}{2} - u), 0 & (\frac{1}{2} - u), (\frac{1}{2} + u), 0 \end{array}$$

where

$$u = 0.160$$

Consequently, it can readily be seen that because of the rearrangement, the θ' -CuAl₂ lattice must expand along the a and b axes from 5.71 to 6.054 Å. and shrink along the c axis from 5.796 to 4.864 Å. In the mechanism proposed here this expansion and shrinkage are considered to be incidental to the placing of the atoms in the proper positions with respect to one another. In other words, for the correct arrangement of atoms the lattice as a whole will readjust itself dimensionally to correspond to the stable form.

As postulated, three stages are required: (1) realignment of copper atoms in θ' -CuAl₂ into a more symmetrical arrangement; (2) a buckle* of aluminum atoms on the (011) planes in the [100] direction to an amount of 0.544 Å.; (3) a buckle, of the same magnitude, of the aluminum atoms that previously were on the (101) planes of the θ' -CuAl₂ lattice, and in the direction that formerly was the [010] direction.

These three stages are illustrated in Fig. 2. In Fig. 2A the structure of θ' -CuAl₂, which was derived previously, is given. By comparing this

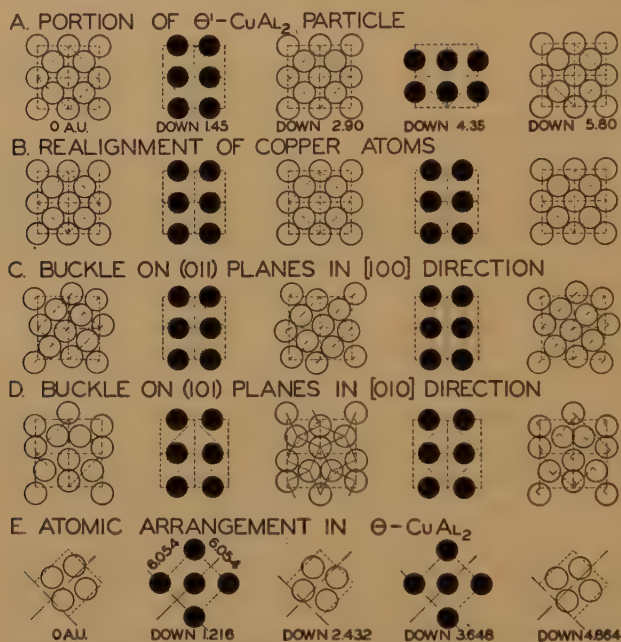


FIG. 2.—ATOMIC POSITIONS FOR THE VARIOUS STAGES IN THE TRANSFORMATION OF θ' -CuAl₂ TO θ -CuAl₂ AFTER PRECIPITATION.
(See explanation under Fig. 1.)

with Fig. 2E, the structure of θ -CuAl₂, it will be seen at once that the planes of copper atoms are exactly the same for the latter phase but that they are different in arrangement for the former, less stable phase. The first stage, therefore, would appear to be the realignment of the copper atoms as postulated. That this does not take place at a later stage is indicated by the fact that the trend of the transformation is to increase the symmetry of arrangement about each of the copper atoms.

The ensuing two stages of buckling, the results of which are shown in Figs. 2C and 2D, are probably accompanied by the expansion and con-

* A "buckle" is defined as a shearing process in which the odd numbered planes move a definite distance in one direction while the even numbered planes move the same distance in the opposite direction.

traction mentioned previously. They must take place separately, since no combination of them into a single stage will give the geometrical positions required by the θ -CuAl₂ structure. The magnitude of the buckle can be computed quite simply as follows:

If x = the magnitude of the buckle,

u = atomic displacement of aluminum atoms in θ -CuAl₂ structure,

Then:

$$\begin{aligned}\frac{a_0\theta}{\sqrt{2}} &= 2(\sqrt{2}u + \sqrt{2}x) \\ \frac{6.054}{4} &= u + x = 0.16 \times 6.054 + x \\ x &= 1.513 - 0.969 = 0.544 \text{ \AA}.\end{aligned}$$

SUMMARY AND CONCLUSIONS

The complete precipitation of θ -CuAl₂ out of the supersaturated solid solution may be considered as taking place in seven stages:

1. Segregation of the atoms in the solid solution by pure chance into groups containing the required number of copper atoms.
2. Realignment of the copper atoms in these groups into a more symmetrical ordered arrangement.
3. Rearrangement of the atoms to form a nucleus of θ' -CuAl₂, probably in a greatly distorted form.
4. Growth and precipitation of θ' -CuAl₂ particles by the formation of an interface.
5. Realignment of the copper atoms in θ' -CuAl₂ into a more symmetrical arrangement.
6. Buckle of aluminum atoms on the (011) planes in θ' -CuAl₂ in a [100] direction to an amount of 0.544 Å.
7. Buckle of the aluminum atoms that were on the (101) planes of the θ' -CuAl₂ lattice in what was previously the [010] direction, to the same magnitude.

Stages 3 and 5 probably will require an appreciable activation energy to start. Stages 3 and 7 will be accompanied by dimension changes.

While the property changes concomitant with the precipitation will be discussed in part II, it may be stated here that maximum hardness will be attained in stage 4 and the alloy will be overaged during the subsequent stages. In low-temperature aging under normal conditions (i.e., excluding the effects of plastic deformation) the alloy probably never gets beyond the beginning of stage 4, except, possibly, after prolonged aging.

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Age-hardening of Aluminum Alloys, IV—Discussion of the Theory

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MEMBER A.I.M.E.

(New York Meeting, February, 1939)

ALTHOUGH age-hardening in an aluminum-base alloy containing magnesium was observed by Alfred Wilm¹ as early as 1911, it was not until 1919 that a theory of the mechanism of age-hardening was proposed. Merica, Waltenberg and Scott,² studying the age-hardening characteristics of Duralumin at the National Bureau of Standards, came to the conclusion that age-hardening of this alloy is caused by the precipitation of CuAl_2 , which is less soluble at the aging temperature than at the solution heat-treating temperature. It was postulated that the initially precipitated particles were of fine colloidal dimensions but that they gradually grew in size. Maximum hardness was assumed to be attained when the particles reached a critical size. This theory was at first received skeptically, since it was a widely accepted view at that time that the solid solution state should represent the hardest state of an alloy.

Shortly thereafter, Jeffries and Archer proposed their well-known "slip interference theory."³ They suggested that age-hardening was accomplished by the precipitated particles acting as keys interfering with slip along crystallographic glide planes. They showed that this mechanical theory led directly to the assumption that maximum hardening would be produced by particles of a critical size, which they suggested would have a diameter approximately 10 times that of the aluminum atom. This contribution amplified and explained so rationally the age-hardening theory of Merica, Waltenberg and Scott that wide acceptance resulted.

OBJECTIONS TO SIMPLE PRECIPITATION THEORY

From time to time certain experimental facts have been cited against the simple precipitation theory. The first of these was the discovery by Fraenkel⁴ that, although the electrical resistivity of Duralumin decreased during aging at higher temperatures (from 100° to 250° C.), it increased during aging at ordinary temperatures. This was not in accordance

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¹ References are at the end of the paper.

with the belief current at that time that resistivity should decrease during precipitation.

It has been pointed out by Portevin and Chevenard,⁵ as well as by other workers, that they were unable to explain volume changes that occurred during age-hardening of some aluminum alloys on the basis of the simple precipitation theory. For example, binary aluminum-copper alloys increase rapidly in density during the very early stages of age-hardening at room temperature. On the other hand, Duralumin first decreases and then increases in density during room-temperature aging. Aluminum-magnesium-silicide alloys show only a decrease in density during room-temperature aging. After extended periods of aging, especially at elevated temperatures, the density of the alloy decreases to a value usually far below that which would be calculated on the basis of a mixture of aluminum and the precipitating phase.

It has been demonstrated by Fraenkel⁶ and others that aluminum-base alloys age-hardened at room temperature suffer an initial decrease in hardness upon subsequent aging at more elevated temperatures. For some time, this behavior received no satisfactory explanation in terms of the simple precipitation theory.

One of the principal objections to the precipitation theory of age-hardening was the lack of direct evidence of precipitation at room temperature, or during the early stages at somewhat higher temperatures. The failure of microscopic and Debye-Scherrer methods carried little weight because neither method could be expected to reveal colloidal particles of the size postulated by the theory. However, failure of the back-reflection X-ray method,⁷ which could determine lattice parameters with such precision that it was assumed small amounts of precipitation could be detected, was undoubtedly the strongest argument advanced against the precipitation theory of age-hardening.

PRE-PRECIPITATION THEORY

As a result of these objections to the simple precipitation theory, several metallurgists have assumed that prior to the formation of crystal nuclei of the second phase there is some kind of change within the solid solution, which causes hardening of the alloy. This pre-precipitation process has been variously assumed to be: (1) local variation in interatomic distances in the neighborhood of solute atoms (by the formation of CuAl_2 molecules⁸ or for some less clearly defined reason⁹), (2) the diffusion of solute atoms to definite positions of the aluminum lattice producing an ordered arrangement,¹⁰ or finally, (3) the diffusion of copper atoms to certain regions forming groups or "knots,"¹¹ which are not sufficiently organized to form a crystal nucleus, but which are sufficiently stable to simulate a nucleus and cause hardening of the alloy by inter-

ering with slip. The last hypothesis, which was ably presented by Dr. Merica when he became convinced that his simple precipitation theory was no longer adequate to explain all the facts, has undoubtedly had the largest following.

The above is a very brief history of the theory of age-hardening in aluminum alloys up to the time when the present authors began their investigation. Early in the course of their work, it was found that the back-reflection X-ray diffraction method was not nearly as sensitive as had been supposed.¹² It could not reveal changes in lattice parameter even though precipitation had progressed to a point where particles could be resolved under the microscope. This immediately nullified the most potent argument against the simple precipitation theory. If this fact had been discovered earlier, it is very unlikely that Dr. Merica would have revised his theory or there would be so many proponents of pre-precipitation theories.

Previous papers of this series¹³ have presented results of investigations which led to the following conclusions:

1. The lattice parameter of aluminum is not changed by the precipitation of minute particles during the early stages of the age-hardening of aluminum-copper or aluminum-magnesium alloys because of the highly localized and heterogeneous nature of the precipitation.

2. In both the aluminum-copper and aluminum-magnesium alloys, precipitation can be observed microscopically before the aging has progressed far enough to change the yield strength and elongation substantially.

3. In both the aluminum-copper and aluminum-magnesium systems, the phase that precipitates during the aging at low temperatures is different from the phase that precipitates at elevated temperatures.

4. The presence of two peaks in the aging curve, which has recently been advanced as an argument in favor of pre-precipitation,^{10,11} is attributable to the fact that precipitation occurs more rapidly in regions that were deformed during the quench than in regions that were not deformed.

5. There now seems to be no justification for modification or complication of the theory of precipitation-hardening originally advanced by Merica, Waltenberg and Scott.

These papers dealt principally with the presentation of experimental data. While some of the objections to the precipitation theory were considered briefly, discussion of the theory was meager. In fact, it became evident during the discussion of these papers and in subsequent informal discussions that the authors had not presented their ideas in regard to the theory with sufficient clarity or in sufficient detail. The object of writing the present paper is to rectify this situation as well as to make a more complete presentation of the precipitation theory than has been given previously.

MECHANISM OF AGE-HARDENING

Solid Solution

Before considering the decomposition of solid solutions, which causes age-hardening, let us consider the state of the solid solution in the temperature range of solution heat-treatment. When aluminum-copper alloys are held for a sufficient length of time at a temperature above that at which all the copper is soluble, the copper goes into solid solution; i.e., the copper atoms are distributed at random on the aluminum lattice. As a result of thermal agitation, the copper atoms are, of course, moving from point to point on the lattice. In any given region, therefore, the concentration of copper atoms is constantly changing. At any given time, there will be some regions where the concentration of copper atoms is high. Such groupings are not stable at this high temperature, and they immediately disintegrate. However, while some of these groups are disintegrating, others will be forming, so that a statistical equilibrium obtains.

If we assume, in accordance with the generally accepted ideas of solid solution, that the solute atoms are distributed individually and collectively at random, the probability of occurrence of various numbers of copper atoms in certain size groups can be accurately calculated by the Poisson Distribution Equation:

$$P_{(J)} = \frac{\epsilon^J e^{-\epsilon}}{J!}$$

where: P = probability of occurrence of a group,

J = number of copper atoms in a group,

$P_{(J)}$ = probability of occurrence of J copper atoms in a group,

ϵ = average number of copper atoms in a group,

e = base of natural logarithms.

Table 1 shows the results of some of these calculations. The probability figures in which we are most interested are those for which the copper and aluminum atoms are present in the proportions of the intermetallic compound CuAl_2 . These probabilities are indicated by an asterisk. It will be noted that as the group size increases, the probability of copper and aluminum atoms occurring in CuAl_2 proportions becomes lower.

Formation of Nuclei

We are now in a position to consider the conditions existing in this solid solution immediately after a rapid quench. The structure that existed at the solution heat-treating temperature is retained, at least momentarily. At the lower temperature, the magnitude of the thermal

vibration of the atoms is relatively low, so that previously mentioned groups of copper and aluminum atoms should be relatively stable (i.e., the tendency to disintegrate by diffusion will be much lower than it was at the higher temperature). Groups having the composition CuAl_2 would be expected to be more stable than other groups, and the larger the group, the more stable they would be expected to be. Above a certain limiting size, these CuAl_2 groups would be expected to rearrange rapidly to form crystals of the precipitating phase, i.e., to form stable nuclei.

TABLE 1.—*Probability of Occurrence of Copper Atoms in Atomic Groups of Various Sizes—Poisson Equation*

ALLOY: 94 ATOMS OF AL + 2 ATOMS OF CU (4.78 PER CENT CU BY WEIGHT)

Number of Cu Atoms, J	Atomic Group Size						
	3 Atoms $\epsilon = \frac{1}{16}$	6 Atoms $\epsilon = \frac{1}{8}$	9 Atoms $\epsilon = \frac{3}{16}$	12 Atoms $\epsilon = \frac{1}{4}$	24 Atoms $\epsilon = \frac{1}{2}$	36 Atoms $\epsilon = \frac{3}{4}$	48 Atoms $\epsilon = 1$
0	0.9394	0.8744	0.8290	0.7788	0.6065	0.4724	0.3679
1	0.0587 ^a	0.1093	0.1554	0.1947	0.3033	0.3543	0.3679
2		0.0068 ^a	0.0145	0.0243	0.0758	0.1329	0.1839
3			0.0009 ^a	0.0020	0.0126	0.0332	0.0613
4				0.00013 ^a	0.0016	0.0062	0.0153
5					0.00016	0.00093	0.0031
6					13×10^{-6}	0.00012	0.0005
7					94×10^{-8}	12.5×10^{-6}	0.00007
8					6×10^{-8a}	11.7×10^{-7}	9×10^{-6}
9						98×10^{-9}	1×10^{-8}
10						73×10^{-10}	1×10^{-7}
11						5×10^{-10}	9×10^{-9}
12						3×10^{-11a}	77×10^{-11}
13							59×10^{-12}
14							42×10^{-13}
15							29×10^{-14}
16							18×10^{-15a}

^a Cu and Al atoms in proper proportion to form CuAl_2 .

Just how large a nucleus of precipitate must be for stability at any given aging temperature is unknown. The fact that the electrical resistivity of an aluminum-copper alloy increases slightly during the early stages of aging at 100° C. (Fig. 1) indicates that the nucleus size is slightly less than the order of wave length of the electrons. Mott¹⁴ estimates the wave length of the conduction electron to be of the order of four or five interatomic distances. Assuming that this estimate is correct, the smallest stable nucleus at 100° C. would contain approximately 48 atoms (16 copper and 32 aluminum).

Table 2 presents probability calculations for groups of 48 atoms in the solid solution at the heat-treating temperature, or immediately after

quenching. It will be noted that there are 22,500 groups per cubic millimeter each containing the proper proportion of copper and aluminum atoms to form CuAl_2 . These groups will precipitate almost immediately, allowing only a brief time for probable rearrangement of atoms

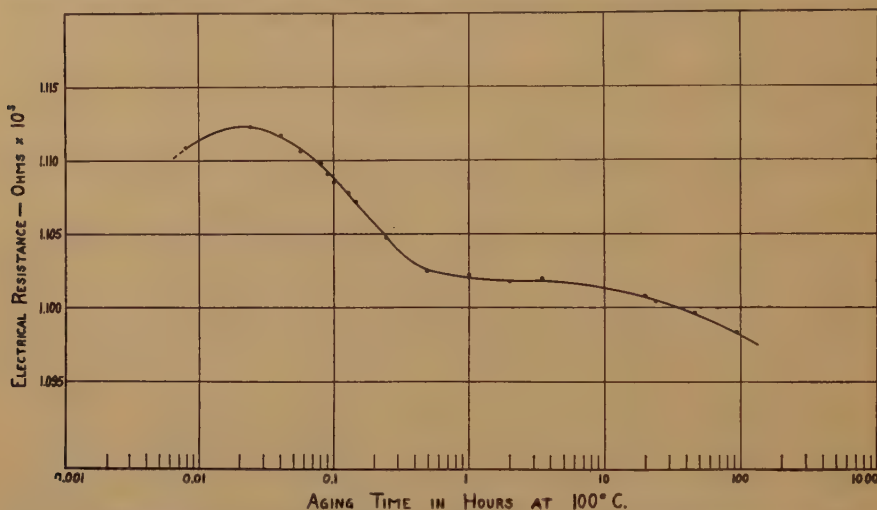


FIG. 1.—EFFECT OF AGING AT 100° C. UPON ELECTRICAL RESISTANCE OF A HIGH-PURITY ALUMINUM-COPPER ALLOY (4 PER CENT CU).

into the proper position for the θ' space lattice. In addition to these groups, all ready to precipitate, there are 362,000 groups each lacking but one copper atom to form a stable precipitate particle. Likewise, there are 5,250,000 groups each lacking but two copper atoms, etc. In

TABLE 2.—Probable Numbers of Groups, Containing a Total of 48 Atoms with Various Numbers of Copper Atoms, in one Cubic Millimeter of an Aluminum-copper Alloy (4.78 Per Cent Cu)

Number of Cu Atoms, J	$P(J)^a$	Number of Groups ^b in 1 Cu. Mm.	Number of Cu Atoms, J	$P(J)^a$	Number of Groups ^b in 1 Cu. Mm.
0	0.3679	46×10^{16}	8	9×10^{-6}	11.3×10^{12}
1	0.3679	46×10^{16}	9	1×10^{-6}	12.5×10^{11}
2	0.1839	23×10^{16}	10	1×10^{-7}	12.5×10^{10}
3	0.0613	76.5×10^{16}	11	9×10^{-9}	11.3×10^9
4	0.0153	19.1×10^{16}	12	77×10^{-11}	96.2×10^7
5	0.0031	38.7×10^{14}	13	59×10^{-13}	74.7×10^6
6	0.0005	6.3×10^{14}	14	42×10^{-13}	52.5×10^5
7	0.00007	8.8×10^{13}	15	29×10^{-14}	36.2×10^4
			16 ^c	18×10^{-16}	22.5×10^3

^a Probability of occurrence of J Cu atoms in a group of 48 atoms.

^b Total number of cells, containing 48 atoms, in 1 cu. mm. = 12.5×10^{17} .

^c Cu and Al atoms in proportion to form one unit cell of θ' .

other words, in the as-quenched condition, there are a large number of potential nuclei for precipitation at approximately 100° C. Obviously, additional potential nuclei form during aging by the chance association of copper atoms in a manner similar to the formation of these groups at higher temperatures.

As lower and lower aging temperatures are employed, it would be expected that the smallest stable nucleus would contain fewer and fewer atoms. That this is true is indicated by the relatively large increase in resistivity upon room-temperature aging compared with smaller increases at higher temperatures. It is also in accord with the theory of nucleation developed by Gibbs¹⁵ and Einstein¹⁶ and confirmed and extended by others.¹⁷⁻²⁰ The size, the formation, and the stability of nuclei will be considered in more detail in connection with subsequent discussion.

Growth of Nuclei

After a stable nucleus or particle has precipitated, it can grow by the normal and simple process of diffusion of copper atoms in solid solution to the interface. As the copper atoms attach themselves to the precipitate particle, the concentration of copper atoms in the adjacent solid solution is diminished. Therefore, diffusion of copper atoms into this region is the normal type of "downhill" diffusion.

EFFECT OF AGING ON PROPERTIES

In the early stages of the aging process, there is a period of time between the instant of quenching and the first measurable hardening, which is generally called the "incubation" period. During this period, nuclei formation and growth are proceeding, as evidenced by changes in electrical resistivity and density. However, the individual particles are relatively small in size and number, and consequently have little effect on the mechanical properties.

Electrical Resistivity

According to the modern theory of the metallic state, maximum electrical resistivity would be expected in an age-hardening alloy when the maximum number of particles have attained a size comparable to the wave length associated with the electron. Consequently, one of the first changes to be observed as the particles grow would be an increase in the electrical resistivity, provided the initial particle size is less than the wave length of the electron. Obviously, as the particles increase beyond this size, the electrical resistivity decreases.

Fig. 2 is a typical curve showing the variation in electrical resistivity of a binary aluminum-copper alloy upon aging at room temperature. During the first two or three hours there is considerable increase in resistivity, indicating that the original nuclei were considerably smaller

than those that formed at 100° C. (see Fig. 1). It is suggested that most of the initial nuclei contain from 12 to 48 atoms. Table 3 gives the number of the smallest suggested groups in each cubic millimeter at the time of quench. At the maximum of the curve the average particle size is that which offers maximum interference to the flow of electrons (such average particle probably containing more than 48 atoms). As

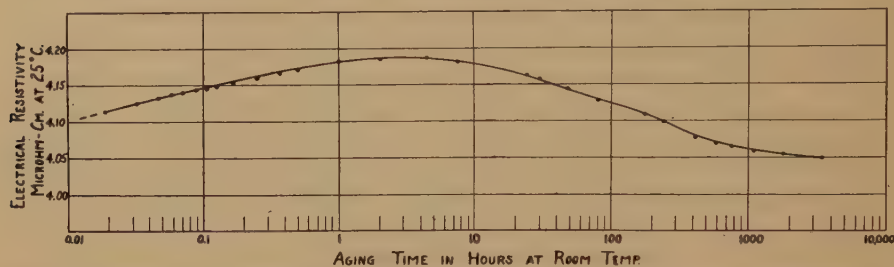


FIG. 2.—EFFECT OF AGING AT ROOM TEMPERATURE UPON ELECTRICAL RESISTIVITY OF A HIGH-PURITY ALUMINUM-COPPER ALLOY (4 PER CENT CU).

the aging progresses further, the particles grow beyond this most effective size and the resistivity decreases.

TABLE 3.—*Probable Numbers of Groups, Containing a Total of 12 Atoms with Various Numbers of Copper Atoms, in One Cubic Millimeter of an Aluminum-copper Alloy (4.78 Per Cent Cu)*

Number of Cu Atoms, J	$P(J)^a$	Number of Groups ^b in 1 Cu. Mm.
0	0.7788	39×10^{17}
1	0.1947	97×10^{16}
2	0.0243	12×10^{16}
3	0.0020	10×10^{15}
4	0.00013	65×10^{13}

^a Probability of occurrence of J Cu atoms in a group of 12 atoms.

^b Total number of groups, containing 12 atoms, in 1 cu. mm. = 50.8×10^{17} .

Specific Volume

There has been an inclination to assume that some of the volume changes that occur during aging cannot be explained in terms of the precipitation theory. It is the opinion of the authors that these volume changes can be explained on the basis of the precipitation theory far more logically and convincingly than on the basis of any pre-precipitation theory that has come to their attention.

The volume change that has been cited most frequently against the precipitation theory is the contraction that occurs when binary aluminum-

copper alloys age at room temperature (Fig. 3). It is generally recognized that a contraction accompanies the formation of the intermetallic compound CuAl_2 . It has, however, generally been assumed that the expansion of the solid solution as a result of copper depletion would more than counterbalance this contraction. A glance at Tables 1, 2 and 3, however, will show that there are a large number of groups of atoms existing in the alloy before and immediately after the quench that require only rearrangement of the atoms to form crystal nuclei of CuAl_2 . This formation of nuclei obviously involves no change in concentration of the solid solution. Obviously, then, the initial change should be a contraction. Formation of other nuclei from groups that require the addition

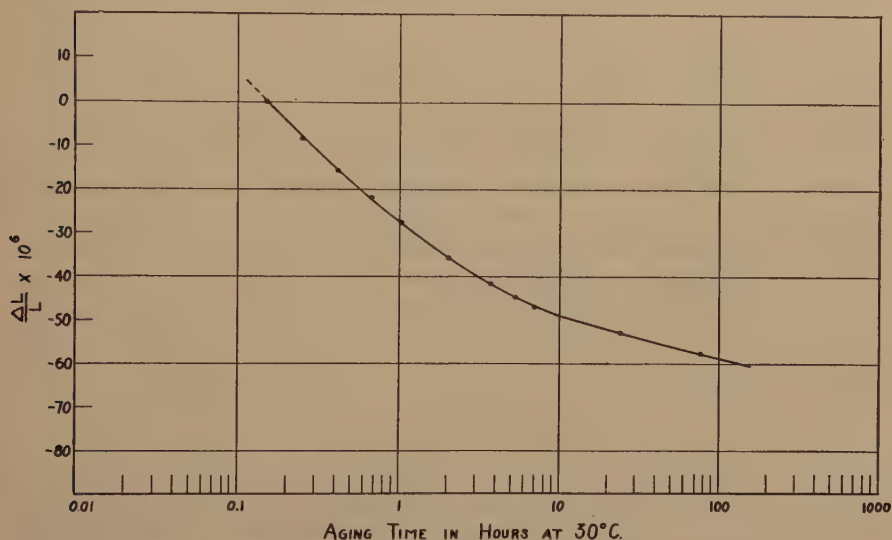


FIG. 3.—CHANGE IN UNIT LENGTH OF HIGH-PURITY ALUMINUM-COPPER ALLOY (4 PER CENT CU) UPON AGING AT 30°C.

of one or more copper atoms raises the problem of calculating the changes in the specific volume of the solid solution as a result of this migration of one or more copper atoms in the solid solution. It also raises the problem of calculating the elastic strain between the particles of precipitate and the surrounding solid solution—especially at the early stages when there is good registry between the lattices of the two phases. Such calculations cannot be made at the present time for lack of necessary data. However, it is the opinion of the authors that a limited formation of nuclei from the incomplete groups would probably result in further contraction.

At higher aging temperatures, where the smallest stable nucleus is much larger, containing perhaps 48 atoms, the contraction caused by the precipitation of groups that exist at the time of quenching is so small that it is not directly measurable. The formation and growth of nuclei

to such a stage that volume changes are readily measurable involve considerable diffusion of copper atoms from the solid solution to the nuclei. This lowers the concentration of the solid solution and tends to cause a volume increase, which sooner or later counterbalances the contraction. This is generally recognized, and on this basis it is possible to calculate accurately the specific volume of aluminum-copper alloys that have been brought to equilibrium at annealing temperatures. However, it has been pointed out that the growth during artificial aging at approximately 150° C. is considerably larger than the calculated value. The authors are still of the opinion, previously expressed, that as soon as the particles of precipitate have grown so large that the lattices of the particles and that of the solid solution cannot register, there is a region of lower density around the precipitate particles. If the particles are sufficiently small and numerous, the volume of this lower-density material would become appreciable and produce a measurably higher specific volume. Moreover, as has been previously pointed out, most of the calculations of volume changes have been made by assuming the form of CuAl_2 that is stable at annealing temperatures (the θ phase), whereas it is now known that the phase precipitating at 150° C. is a less dense form of CuAl_2 (the θ' phase).

Other unexplained volume changes, which occur in very complex alloys where several phases can precipitate and many reactions can occur, do not merit consideration here, but can in all probability be explained similarly.

Mechanical Properties

The crystal nuclei, which form and grow during the incubation period, finally reach a sufficient size in sufficient numbers to interfere appreciably with slip; i.e., they harden the alloy. Both the formal and the informal discussions that have followed the presentation of parts I, II and III of this series have indicated that there is some misunderstanding on this point. Many have erroneously obtained the impression that the authors attribute hardening to the microscopically resolvable particles. On the contrary, emphasis has been placed on the microscopic detection of precipitation merely to establish that precipitation takes place at a very early stage—before any appreciable hardening occurs. The authors agree with early statements by Merica, Waltenberg and Scott and by Jeffries and Archer that particles of colloidal size are most effective in hardening.

When the precipitate particles grow beyond the critical size, softening occurs. The critical size varies somewhat for different mechanical properties (tensile strength, yield strength, hardness and elongation), but in aluminum alloys an average particle size in the microscopic range (i.e., greater than 1000 Å.) produces overaging or softening.

The initial softening that occurs on artificial aging, subsequent to aging at a lower temperature, can be adequately explained in the following manner. At low temperatures, many small nuclei form and never grow to a size that is stable at the elevated temperature. Consequently, the first effect of the high temperature is to cause disintegration or resolution of the precipitate particles. Obviously, this would soften the alloy. A similar explanation was presented by Masing,¹⁸ but he then felt that it was necessary to assume the formation of "knots," which were endowed with the same stability as nuclei. The injection of this complication is unnecessary because it is now known that nuclei, or much larger precipitate particles, can form without being detected by the X-ray back-reflection method.

DETECTION OF PRECIPITATE

In the past, much weight has been given to the inability of X-rays to reveal precipitate during the early stages of aging. However, careful consideration of the small size of particles that exist during the early stages of aging, and the mechanism by which they are formed, will show that the Debye-Scherrer and back-reflection methods could not be expected to reveal the precipitation. The Debye-Scherrer method will ordinarily not reveal a second phase unless it is present to the extent of 1 per cent or more in the form of relatively large, well-formed crystals. One would, therefore, expect that the deformed crystals of colloidal size, which form during the early stages of aging of aluminum-copper alloys, would have to constitute several per cent of the alloy in order to be revealed by the Debye-Scherrer method. When the specimens have overaged at elevated temperatures, Debye-Scherrer patterns of the precipitate can be obtained. Such patterns are useful in identifying the precipitating phase.

The back-reflection method, on which so much reliance was placed, measures the lattice parameter of the solid solution, and could not be expected to detect precipitation unless the precipitation were accompanied by a measurable change in the parameter of the solid solution. Obviously, the initial precipitation—i.e., the formation of nuclei from the groups of atoms that already exist at the time of quench—produces no change in the parameter of the adjacent solution except for an immeasurable elastic strain. As the nuclei grow, the solid solution is depleted in copper in the immediate vicinity of these nuclei. There is, of course, a tendency for the parameter to change through this minute volume. However, since the precipitate particles are formed by the Widmanstätten mechanism, so clearly elucidated by Dr. Mehl and his co-workers,²¹ there will be elastic stress in the particle and in the solid solution to maintain fairly good registry between the lattices of the two phases. During this period, no change in lattice parameter could be detected by the back-

reflection method. Finally, the precipitate particles become so large that registry cannot be maintained between the crystal plane of the CuAl_2 and the solid solution crystals. Even at this stage, the solid solution is depleted in copper only locally in the vicinity of the precipitate particles. Moreover, the concentration of the solution in these depleted regions varies from almost 0 per cent Cu to the full concentration of the solid solution. Since the back-reflection method will not reveal small percentages of a second phase, it could not be expected to reveal reflections from the regions depleted in copper, until there existed a fairly large volume of solid solution of a given concentration. It has, in fact, been shown experimentally that the back-reflection method will not reveal any change in parameter until long after the precipitation can be revealed microscopically.¹²

Of course, the ordinary optical microscope will not resolve the particles of colloidal size that precipitate during the early stages of aging of aluminum-copper alloys. However, these particles precipitate preferentially in regions that have been plastically deformed during quenching in cold water; i.e., along the grain boundaries and the slip bands.¹³ In this way, a readily discernible pattern is produced, which can be revealed by suitable methods of polishing and etching.²² The stage of aging at which this pattern can be revealed depends to a large extent upon the skill with which the specimen is polished and etched.

CONCLUSIONS

A correlation of existing experimental data on age-hardening of aluminum alloys has led to the following conclusions, which are consistent with the precipitation theory originally proposed by Merica, Waltenberg and Scott:

1. Age-hardening results from the controlled decomposition of a supersaturated solid solution.
2. This decomposition is accomplished, as in other systems, by means of the formation of nuclei of a second phase and the growth of these precipitated particles.
3. The nuclei form by the normal process of chance grouping of solute atoms, and Widmanstätten precipitation.
4. Growth of the precipitated particles occurs by the usual process of crystal growth.
5. The changes in physical and mechanical properties are explained in terms of this normal precipitation process.

ACKNOWLEDGMENT

The dilation and resistivity curves presented in this paper are a part of some unpublished work by Mr. L. A. Willey. The authors hereby express their thanks for the use of these data.

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DISCUSSION

(John T. Norton presiding)

B. W. GONSER,* Columbus, Ohio.—Studies on the age-hardening of aluminum alloys have been a valuable contribution to theoretical metallurgy. Nevertheless, from the broader viewpoint of age-hardening in general, I should like to see more work done on other alloy systems that exhibit a similar behavior. In other words, a general explanation of age-hardening phenomena can be built only by combining studies of all alloys, or at least representative alloys, that exhibit this behavior. Such studies appear necessary to maintain a proper balance or perspective.

D. K. CRAMPTON,† Waterbury, Conn.—The authors have presented some interesting data on the probability of various sizes of groups of copper and aluminum atoms being present in certain alloys. A tacit assumption has been made that only when these groups contain the theoretical proportion of copper and aluminum atoms

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to form the compound CuAl_2 will there be any precipitation of such groups. If I have interpreted their thought correctly, I would disagree with this assumption. It would seem to me possible, and in fact probable, that incomplete or imperfect groups could well precipitate. If such incomplete groups did precipitate, it would seem that the probability of any given such group precipitating would be an increasing function of the degree of perfection of the group. In other words, the more nearly complete or perfect the group, the greater the probability of its precipitating. This concept should be given consideration in the broad problem of probability of precipitation.

M. L. V. GAYLER,* Teddington, England.—Messrs. Fink and Smith have omitted to refer to two recent and most important researches, based on the X-ray examination of copper-aluminum alloys, which have been published independently and simultaneously by Calvet, Jacquet and Guinier^{23,24} in Paris and by my colleague, G. D. Preston.²⁵ Their results show that during the initial stage of aging segregation of copper atoms occurs on (100) planes, resulting in the formation of thin plates, which vary in size and thickness with the aging temperature. At higher aging temperatures, these investigators found that the phenomena in the X-ray photogram associated with the formation of these copper segregates are gradually replaced by those signifying the appearance of the "intermediate" phase, originally discovered by Wassermann and Weerts.²⁶ Depending on time and temperature, further aging results in other diffraction effects that indicate the presence of CuAl_2 . These facts confirm the existence of the first stage of aging as suggested in my theory of aging.²⁷ From his data, Preston was unable to determine whether the intermediate phase, which he found to be of the calcium fluoride type, could be regarded as a metastable "intermediate" phase or the stable form of CuAl_2 at low temperatures. I have carried out microscopic analyses of a 4 per cent copper-aluminum alloy aged at high temperatures and have obtained evidence, shortly to be published in the *Proceedings* of the Royal Society, that the change from the intermediate phase to the stable form of CuAl_2 is polymorphic. These experimental facts prove definitely that CuAl_2 , as such, is not precipitated from the solid solution during aging.

Messrs. Fink and Smith consider that the two peaks in the aging curve may be "attributed to the fact that precipitation occurs more rapidly in regions that were deformed during the quench than in regions that were not deformed." It is well known that aging may be accelerated by deformation but the authors have produced no experimental facts in support of their suggestion.

I have obtained data (which will be published shortly) on the prolonged aging of 4 per cent copper-aluminum of high purity at temperatures from 0° to 450°C., and the results show that the first stage of aging depends on the temperature and also on the duration of aging. Furthermore, there is a straight-line relationship between the reciprocal of the absolute temperature and the time between the first maximum hardness and the beginning of the increase in hardness to the second maximum. These facts do not support the present authors' view that quenching stresses, which may vary considerably from specimen to specimen, are responsible for two hardening maxima in the aging curves.

* National Physical Laboratory.

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W. L. FINK AND D. W. SMITH (authors' reply).—In regard to the question concerning the accuracy of Poisson's distribution equation, we believe that just below the solidus the solute atoms are distributed at random, or nearly so. In other words, at this temperature, Poisson's distribution equation should give a good approximation to

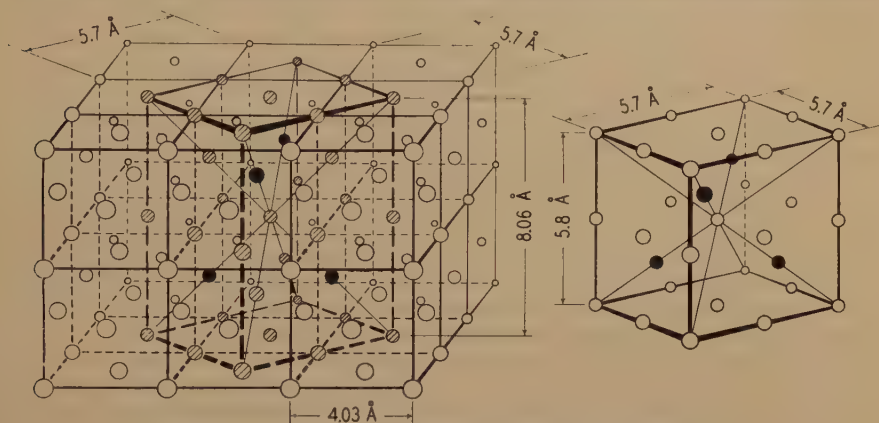


FIG. 4.—ALUMINUM-COPPER SOLID SOLUTION BEFORE AND AFTER PRECIPITATION.

actual conditions. At lower temperatures, where thermal agitation is less, the attractive forces between atoms would have more effect, and Poisson's distribution equation would give poorer and poorer approximation as the temperature decreases (i.e., there should be a greater number of larger groups). A really accurate distribution equation should contain temperature as one of the variables. The equation developed by Einstein, and referred to in the paper, does take temperature into consideration and should be more accurate, at least at the lower temperatures than Poisson's distribution equation. However, the authors have not been able to apply this equation.

In any case, a precise correspondence between the calculated values and the actual values is of minor importance. The important point is to give a picture of the solid solution and to get everyone to realize that there exists naturally in the solid solution groups of atoms of the right size having copper and aluminum atoms in the right proportion to form precipitate particles of θ' .

Our work was done before the appearance of the excellent papers by Preston and by Guinier et al. We have been able to produce patterns of the same type as those reported by them. The facts can be interpreted easily in terms of the theory presented in this paper. The left-hand figure on Fig. 4 shows aluminum-copper solid solution, which contains a group of atoms ready to precipitate. The copper atoms are shown as the filled-in circles, whereas the aluminum atoms are shown either as the open circles or the crosshatched circles. The crosshatched circles represent the

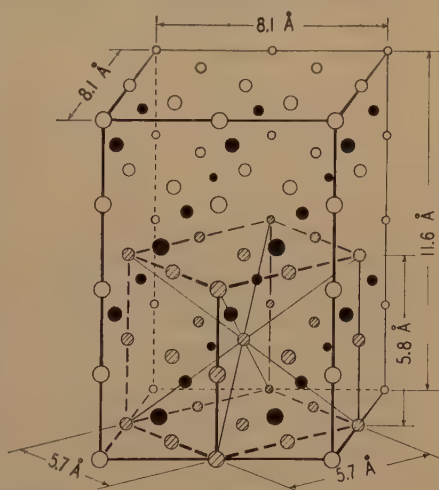


FIG. 5.—RELATION BETWEEN UNIT CELLS.

aluminum atoms within, or on the boundaries of the region that will form one unit cell of θ' . The figure on the right shows the unit cell of θ' after precipitation. Fig. 4 was based upon the dimensions and orientation relationships reported by Preston. Wassermann and Weerts²⁸ previously reported the same phase (θ') but selected the unit cell differently. Fig. 5 shows the relation between the two unit cells. The dimensions marked on the figures were obtained from X-ray patterns of much larger precipitate particles than those shown. The elastic strains on a particle as small as that shown here should produce some variation in the dimension c_0 . Since there is good coincidence between the basal planes of the θ' lattice and the cube planes of the solid solution lattice, growth of the nucleus can occur readily parallel to the (100) plane. Since registry is not good along the c axis of the θ' phase, growth in this direction would be impeded. Platelets of precipitate formed in this manner would be expected to produce the streaks obtained by X-ray methods reported by Guinier and Preston.

Assuming that Fig. 4 accurately represents the conditions, an interesting possibility is presented of calculating the volume change that would be expected during the early stages of aging at room temperature.

In calculating the number of groups of atoms of different sizes for presentation in the paper, the assumption was made that the ratio of CuAl_2 existed in the potential nuclei. The relations shown in Fig. 4 indicate that the number of groups should be calculated on the basis of 16 atoms instead of 12, because 4 aluminum atoms are eliminated from the nucleus during precipitation. Table 4 was calculated on that

TABLE 4.—*Probable Numbers of Groups, Containing a Total of 16 Atoms with Various Numbers of Copper Atoms in One Cubic Millimeter of an Aluminum-copper Alloy (4.78 Per Cent Copper)*

Number Cu Atoms, J	$P(J)$	Number of Groups in 1 Cu. Mm.
0	0.7165	27×10^{17}
1	0.2388	91×10^{16}
2	0.0398	15×10^{16}
3	0.0044	17×10^{15}
4	0.00037	14×10^{14}

basis. Using these values as a basis, the volume changes can be calculated as follows:

The volume of a 16-atom group in Al solid solution = $5.7 \times 5.7 \times 8.06 = 261.87 \text{ \AA}^3$
 Since 4 of the Al atoms are divorced from this group, subtract 65.45

Volume of one unit cell $\theta' = 5.7 \times 5.7 \times 5.8 =$ 196.42
188.44

Decrease in volume on precipitation of one unit cell of $\theta' =$ 7.98 \AA^3

There are 14×10^{14} 16-atom groups per cu. mm. each containing four copper atoms. Therefore, the total decrease in volume during precipitation of these groups = $14 \times 10^{14} \times 7.98 = 11.2 \times 10^{15} \text{ \AA}^3$ per cu. mm. or

$$\frac{11.2 \times 10^{15}}{10^{21}} = 11.2 \times 10^{-6} \text{ cu. mm. per cu. mm.}$$

²⁸ *Metallwirtschaft* (1935) **14**, 605.

or the change in length will be 3.73×10^{-6} m. per m. This corresponds to approximately 6 per cent of the total change in length experienced in 100-hr. aging time according to the curve of Fig. 3.

There are 17×10^{15} 16-atom groups per cu. mm. lacking but one Cu atom to be a stable nucleus. If these gain the required Cu atom and precipitate, the decrease in volume (neglecting effect of diffusion of this atom from solid solution) would be

$$\frac{7.98 \times 17 \times 10^{15}}{10^{21}} = 135.7 \times 10^{-6} \text{ cu. mm. per cu. mm.}$$

or the change in length will be 45.2×10^{-6} mm. per mm. (approximately 75 per cent of total change). Somewhat over 80 per cent of the length change shown in Fig. 3 is therefore accounted for without assuming the formation of new atom groups by chance diffusion at the aging temperature.

In regard to Dr. Crampton's suggestion that incomplete groups may precipitate, it seems to us that this may very well occur when the groups are large; i.e., several unit cells of θ' . It seems rather improbable, however, that a stable precipitate particle could be formed from a group of 12 atoms containing only 3 copper atoms (i.e., when one unit cell is the smallest stable nucleus). Our object in presenting estimates of the number of atomic groups was to show the large number of groups available for precipitation, and we ruled out incomplete groups to avoid controversy. However, if Dr. Crampton is correct, our figures are obviously too low.

When Dr. Gayler refers to "CuAl₃, as such" she evidently refers to the phase in equilibrium at elevated temperatures (θ). The authors have repeatedly stated that it is not the θ phase that precipitates at ordinary aging temperatures, but the phase θ' .

As Dr. Gayler points out, no facts were presented in this paper to support the statement in regard to two peaks in the aging curve being attributable to the fact that precipitation occurs more rapidly in regions that were deformed during the quench than in regions that were not deformed. These facts were presented in the third paper of this series:²⁹

(1) The occurrence of the first peak was coincident with precipitation along grain boundaries and slip planes as revealed microscopically.

(2) Samples that had been quenched slowly enough to avoid visible plastic deformation do not show the first aging peak, and visible precipitation does not occur until later in the aging cycle.

In the last paragraph of Dr. Gayler's discussion, she erroneously attributes to the authors a theory that quenching stresses are responsible for two hardening maxima. The authors have never attempted to correlate internal stresses produced during quenching or otherwise with the shape of the age-hardening curve. It seems doubtful whether any such relation exists. It is the plastic deformation that occurs at grain boundaries and along slip bands during the quench that accelerates the aging as explained in the third paper of this series, but obviously the internal stress remaining in a plastically deformed material is no measure of either the local deformation or the integrated deformation that has occurred.

²⁹ W. L. Fink and D. W. Smith: Age-hardening of Aluminum Alloys, III—Double Aging Peaks. *Trans. A.I.M.E.* (1938) **128**, 223.

The Structure of Aluminum after Compression

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A.I.M.E.

(Chicago Meeting, October 1939)

SINCE 1925, when the preferred orientations in compressed aluminum were first determined^{1,2} the orientations have been described as a fiber texture in which a face diagonal, [110], of the face-centered cubic lattice is parallel to the compression axis. Subsequent experiments have seemed to confirm this texture,³⁻⁵ and a number of theories (recently summarized in references 6 and 7) have been proposed to explain it and to relate it to the behavior of single crystals during compression.^{3,8-11}

The experiments reported in this paper prove that the orientations are not adequately described as quoted above—i.e., as a [110] fiber texture—although this is a first approximation to the actual texture. They also show that the texture cannot be thought of as a stable orientation that is reached and maintained after a sufficient amount of deformation. The actual texture, when studied in detail at successive stages of compression, indicates that a hitherto unsuspected range of orientations is present, both in the polycrystalline metal as a whole and in various individual grains in its interior, and that a state of dynamic equilibrium exists within this range. The reasons for the failure of previous theories to predict the actual texture become obvious when the heterogeneous nature of the flow is considered.

In addition to the deformation texture, the manner of its development, and its theory, this paper presents data on the following related subjects: the identity of strain markings in aluminum; the orientation changes in aluminum single crystals during compression and a comparison of these with the conditions in individual grains of a polycrystalline specimen; the origin of asterism in deformed single crystals, which heretofore has been regarded as a distortion localized at the surfaces of slip planes; and the relation of plastic strain in individual grains in an aggregate to the strain of the whole.

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¹ References are at the end of the paper.

EXPERIMENTAL PROCEDURE

Material.—All experiments were made with high-purity aluminum (99.95 per cent and better), whose purity was verified by spectroscopic comparison with aluminum of known composition. Polycrystalline blocks with grains of a size suitable for the study of individual grains were prepared by casting, rolling to a reduction of 7 per cent, and then annealing 4 hr. at 300° and 15 hr. at 500° C.

Orientation Determinations.—The usual X-ray diffraction methods were employed: back-reflection Laue exposures for initial orientations; and for the deformed crystals, reflection patterns with cobalt or molybdenum radiation, rotating crystal exposures with molybdenum radiation, or transmission Laue photographs with tungsten radiation. In addition, a technique of orientation determination was perfected, using etch pits and a two-circle optical goniometer. The etchant was 9 parts HCl, 3 parts HNO₃, 2 parts HF and 5 parts H₂O, and was used at room temperature. The etching time was adjusted by trial and error on each specimen to give etch pits whose faces were accurately parallel to cube faces. The goniometer was designed to minimize multiple reflections from the etch-pit sides, and its telescope permitted the scintillations from individual etch pits to be distinguished from the general noncrystallographic sheen. The accuracy of the optical method was determined by comparison with back-reflection Laue photographs of undeformed grains and was about 1°—all that was needed for plotting on an 18-cm. stereographic net. Features of the deformation mechanism that would have required a prohibitive amount of labor by X-ray methods were readily studied by this method.

Method of Compression.—The compression of polished blocks was carried out between polished plates in a series of steps with frequent lubrication, in the manner used by Taylor and Farren,⁸ to reduce friction at the compressed surfaces. For reductions in excess of 85 per cent, this was followed by passes in different directions through small rolls, "compression rolling."¹²

DEFORMATION TEXTURE OF POLYCRYSTALLINE ALUMINUM

The deformation texture was determined in two ways: by optical reflection, and by X-ray diffraction. A pair of polycrystalline blocks, shown in Fig. 1, were placed together, compressed in 39 steps to 84 per cent reduction in thickness, separated, and the inner faces etched. Fifty small regions, about 1 mm. in diameter, were marked out at random on the inner faces (avoiding the edges of the blocks). The mean orientation of each of these regions was then determined. The results are shown in Fig. 2, in which the compression axis for each small area is plotted as a

circle in a unit stereographic triangle representing the deformed lattice orientation.¹³

The compression texture of Fig. 2 was confirmed by X-ray diffraction, using cobalt characteristic radiation directed upon the compressed surface at the various angles suitable for reflection from (111), (200), (220), and (311) planes lying in the plane of the compressed sheet, while the sheet was shifted and rotated in its own plane. The texture of fine-grained aluminum reduced 98.6 per cent and 99.9 per cent by compression followed by compression-rolling was not appreciably different from the texture at 84 per cent. The results for 99.9 per cent reduction are plotted in Fig. 3, in which the limits of the orientations for which the reflections

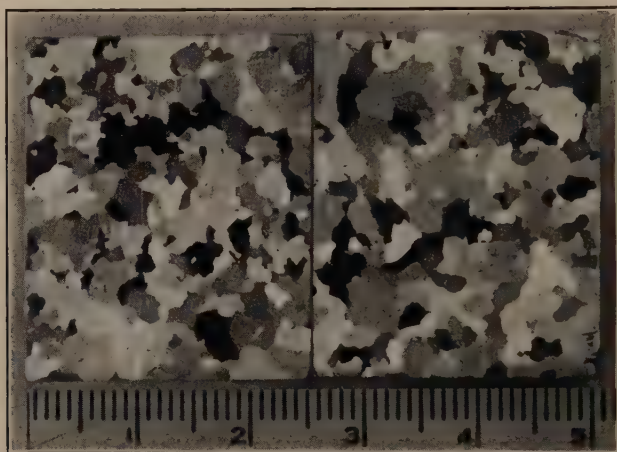


FIG. 1.—INNER FACES OF ALUMINUM BLOCKS BEFORE COMPRESSION.

Etched in HCl , HNO_3 , and HF . Grains studied ranged in area from $\frac{1}{8}$ to 16 mm^2 . Centimeter scale shown below.

are strong, medium, weak, very weak, and none (S , M , W , VW , N) are drawn as arcs of circles about the poles of the reflecting planes (111), (100), (110), and (311), since the exact boundaries were somewhat indefinite and could not be determined with precision.

The X-ray patterns show somewhat more decisively than the optical method the absence of material around [111], the near-absence around [100], the concentration around [110], and the spread from [110] to [311]. It must be emphasized that the evidence for the large spread through the central region of the triangle is incontestable, for it is as positive with the X-ray method as with the optical method. The evidence consists of a long arc of medium intensity on the (311) diffraction ring when the cobalt radiation is incident at or near the Bragg angle for this plane. On some patterns there were indications of a moderately intense clustering near the [311] position (on the hypotenuse of the triangle of Fig. 3), but as this was not confirmed by all the patterns it has not been differentiated from the central region of medium intensity.

From Figs. 2 and 3, it will be seen that the compression texture is only roughly approximated by the statement, appearing uniformly throughout the literature, that it is a $[110]$ fiber texture. Judging from distribution in Fig. 2, fully half of the crystallites are more than 10° or 15° from the $[110]$ orientation at 84 per cent reduction, and the X-ray work shows that this distribution is practically unchanged by a reduction 99 per cent greater (a total of 99.9 per cent). Furthermore, this spread of orientations is not a uniform scatter in all directions from $[110]$, for it avoids orientations within about 20° of $[111]$ and 15° of $[100]$, yet does not avoid orientations near $[311]$.

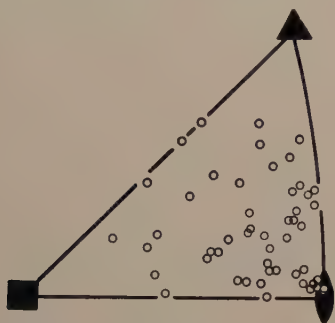


FIG. 2.

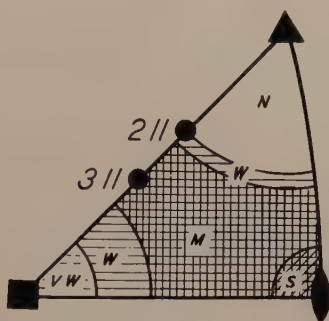


FIG. 3.

FIG. 2.—ORIENTATIONS ON INNER FACES OF BLOCKS AFTER 84 PER CENT COMPRESSION. OPTICAL DETERMINATION.

Orientations of compression axis of randomly chosen areas, about 1 mm. in diameter, are indicated by small circles in standard stereographic projection triangle bounded by directions $[001]$ (\square), $[111]$ (\triangle), and $[011]$ (\circ). Note absence around $[100]$ and $[111]$ and wide, unsymmetrical scatter around $[110]$.

FIG. 3.—ORIENTATIONS IN ALUMINUM COMPRESSION-ROLLED 99.9 PER CENT. X-RAY DETERMINATION.

Concentrations of orientations, as deduced from intensity of X-ray lines, are labeled strong, medium, weak, very weak, and none (S , M , W , VW , N). Note similarity with Fig. 2 in spite of 99.4 per cent greater reduction.

DEFORMATION OF INDIVIDUAL GRAINS

For a thorough understanding of the nature of the deformation texture and how each grain contributes to it, a study of the orientation history of individual grains in the interior of a polycrystalline block is required. The following experiment filled this need. The two blocks of Fig. 1 were compressed in a number of steps, separated, and etched, and the orientations of selected grains on the two surfaces that had been in contact with each other were determined by the optical goniometer. Photographs were taken to aid in identifying the selected grains, and the procedure was then repeated with additional compression.

Range of Orientation

It was found that the grains did not rotate as units with undistorted lattices, but invariably became distorted with a range of orientations that became greater as deformation progressed. Beyond 30 per cent

reduction in thickness it was no longer possible to measure accurately the mean orientation of a grain in the optical goniometer. A fairly good measurement of the orientation range and the mean rotation was obtained, however, by dividing each grain into about six areas and determining the orientation of each of these areas. The compression axis for each area was then plotted on a standard stereographic projection and an envelope was drawn around the points thus plotted, leaving a margin of two or three degrees between the points and the envelope to allow for the spread in orientation within each area. The projections are reproduced in Fig. 4 with the range of orientation of the compression axis shown in the triangle near the center of the circles. The percentage of reduction in thickness is indicated for each envelope. Further information was obtained by plotting on the same projection the direction of an edge of the block relative to the orientation of the lattice in each area. This information (from which may be determined the extent of the azimuthal spread around the compression axis) appears in Fig. 4 near the circumference of the projections.

The spread in orientation is usually much greater than the average rotation of the fragments* of a grain; typical grains spread 7° to 10° at 10 per cent reduction in thickness, two to three times this at 30 per cent, and four to five times this at 60 per cent. The spread appeared to be greater in grains on the inner faces than in grains at the surfaces in contact with the lubricated compression plates, but it is considerable in all grains, both large and small. Fig. 4b is for a grain that originally intersected the surface in two areas of $\frac{3}{4}$ sq. mm. each, separated by a different grain 2 mm. wide. After 31 per cent reduction these areas had rotated into quite separate ranges of orientation, which are connected with dashed lines in the projection to indicate that intermediate orientations doubtless exist in interior portions of the grain. Figs. 4a and 4f are for grains whose exposed areas were originally between 12 and 15 sq. mm.; Figs. 4c, 4d, and 4e are for grains of intermediate size.

At 59 per cent reduction there is only a limited spread in azimuth; at 83.9 per cent this had increased somewhat, and the structure had become so confused that the original boundaries could no longer be determined with certainty. Even in specimens compression-rolled to a reduction of 99.9 per cent, however, transmission Laue patterns did not show a complete fiber texture with all orientations around the axis.

Direction of Lattice Rotation

A reasonably good determination of the average orientation of a distorted grain could be made directly in the goniometer for deformations

* The term fragment is used in this paper to mean any portion of a distorted grain within which the orientation is substantially uniform.

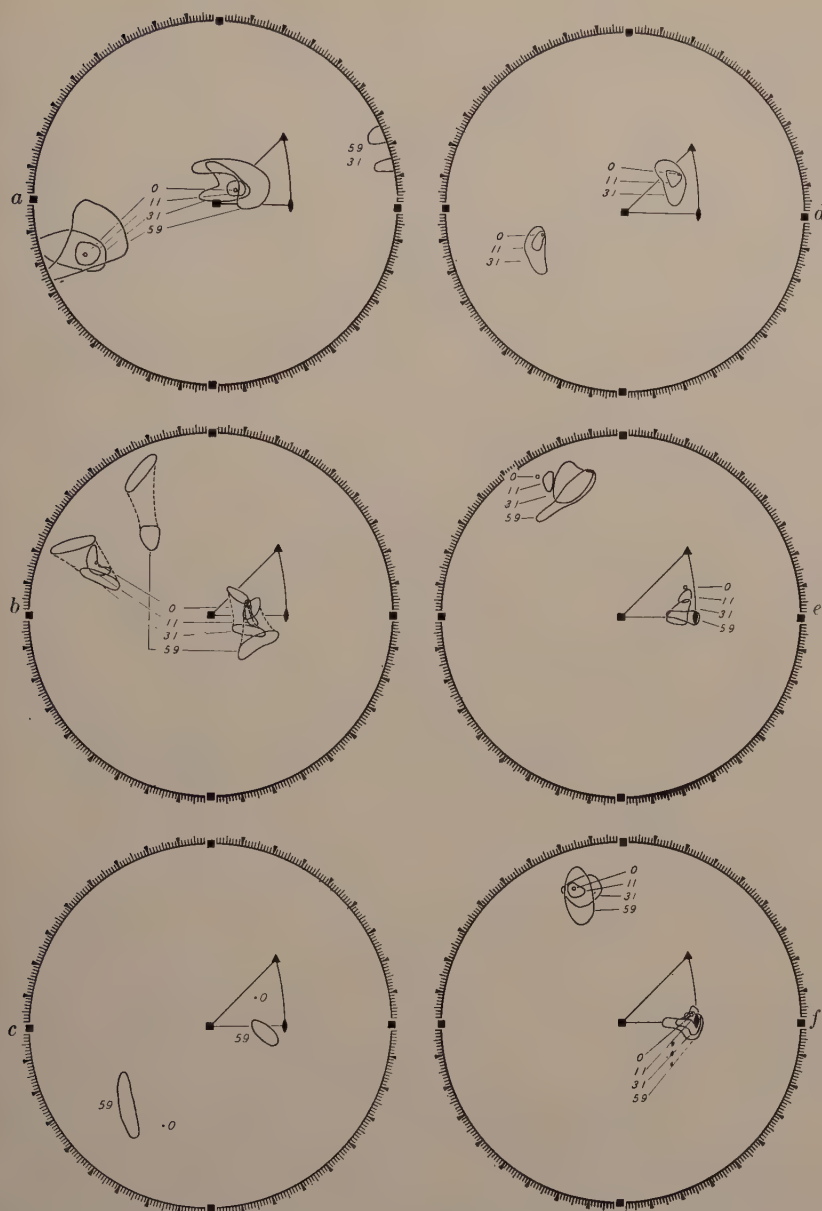


FIG. 4.—RANGE OF ORIENTATION IN SIX INDIVIDUAL GRAINS OF POLYCRYSTALLINE ALUMINUM AFTER VARIOUS STAGES OF COMPRESSION. OPTICAL DETERMINATION.

Initial compression directions are plotted in triangles of standard stereographic projection. Envelopes in triangles contain ranges of orientation of compression axis after compression, indicated in per cent by numbers. Envelopes near circumference of projection indicate ranges of orientation of reference line in compression plane.

of 11 and 31 per cent. The data for the lattice rotation in 25 grains at these deformations are plotted in the stereographic triangle of Fig. 5. In the early stages of compression there appears to be a strong tendency for the compression axis to rotate away from the $[\bar{1}11]$ orientation, and a lesser tendency to leave the $[001]$; a marked tendency to rotate toward the bottom of the triangle, and a smaller tendency to approach the $[011]$ orientation. Thus the axis of compression tends to approach the (100) plane rapidly and the $[011]$ direction more slowly.

Figs. 4 and 5 clearly indicate that grains with the same initial orientation may rotate in different directions under the influence of the applied force and the anisotropic flow of adjacent material. It is evident from



FIG. 5.

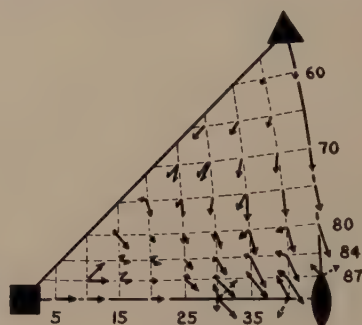


FIG. 6.

FIG. 5.—ROTATION OF GRAINS IN POLYCRYSTALLINE ALUMINUM WITH COMPRESSION. Orientations of compression directions initially, after 11 per cent and 31 per cent compression, are indicated respectively by origins of arrows, intermediate solid circles, and arrowheads. General trends are downward and to the right; i.e., the compression axis seeks the (100) plane and the $[110]$ direction.

FIG. 6.—THEORETICAL ROTATION OF GRAINS IN POLYCRYSTALLINE ALUMINUM WITH COMPRESSION ACCORDING TO G. I. TAYLOR.

Lengths of arrows correspond to compression of aggregate of approximately 3 per cent. Double arrows correspond to two equally favored sets of five slip systems; any rotation whose direction lies between them could equally well occur.

these experiments that the compression texture of aluminum is not a stable orientation or even a group of stable orientations, but is to be regarded as a range within which the orientations of grains and their fragments move about continuously as deformation proceeds. Presumably there is a tendency to rotate in the manner described in the preceding paragraph, but neighboring fragments cause perturbations, which tend toward disorder and establish a dynamic equilibrium that constitutes the deformation texture. Recent theoretical calculations by Taylor for the rotations accompanying the compression of polycrystalline aluminum are summarized in Fig. 6 and are discussed at the end of this paper.

Inhomogeneity of Deformation

The inner faces of the compression blocks became roughened by deformation, as shown in the photographs of the pair of blocks after

22 per cent compression, Fig. 7. The photograph at the left shows the faces that were in contact with each other, after they had been painted to obliterate etching effects. The irregularity of the surface of contact may also be seen from the end view of the pair of blocks, at the right. The heterogeneous flow of which this is proof is important to an understanding of the nature of lattice rotations in aggregates, for it means that each grain and each fragment of a grain deforms in a manner influenced by the everchanging flow of its neighbors, rather than in a simple manner that could be calculated from the behavior of single crystals under the assumption of homogeneous deformation.

Deformation Bands

Many grains develop well-defined bands that extend across the grain in parallel sets. Their appearance in large-grained aluminum may be

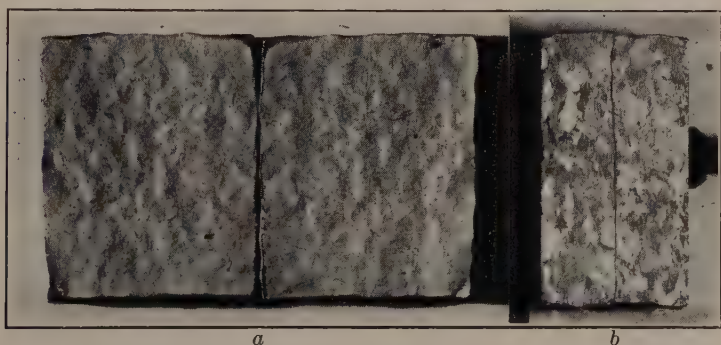


FIG. 7.—POLYCRYSTALLINE BLOCKS AFTER 22 PER CENT COMPRESSION.
(a) Inner surfaces showing rumpling. Blocks separated by rotation about common edge. (b) Side view showing fit at interface.

seen from Fig. 8 and in a grain cut out of this specimen in Fig. 9. When first seen they are straight, but they become curved after further compression. The orientation difference across the boundaries of a band is only a few degrees when the band is first visible, but increases with deformation; thus the bands do not have the relations characteristic of twinning. The material on each side of a band boundary appears always to have a cube plane in common, whereas a twin would have certain other planes in common but not cube planes. A third proof that they are not deformation twins is given by the plane on which they form. In no case were they found with boundaries along (111) planes; in the cases completely analyzed the bands followed (100) planes, but it is possible that they also form on some other plane in the [001] zone, such as (110). The bands are thus of a type similar to the deformation bands in iron^{12,14} and may properly be called deformation bands, but should not be called twins.

Deformation bands contribute to the spread in orientation discussed in an earlier section, but they are not the sole cause of this spread, since there often exists a continuously varying orientation from one point to another in a grain within the bands, or in the absence of bands. In fact,

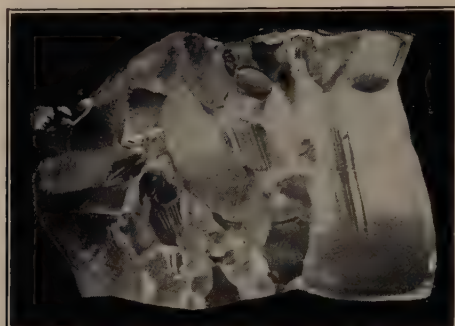


FIG. 8.—LARGE-GRAINED ALUMINUM COMPRESSED 44 PER CENT. $\times 1$.
Deformation bands, still fairly straight, are visible in several of the grains.

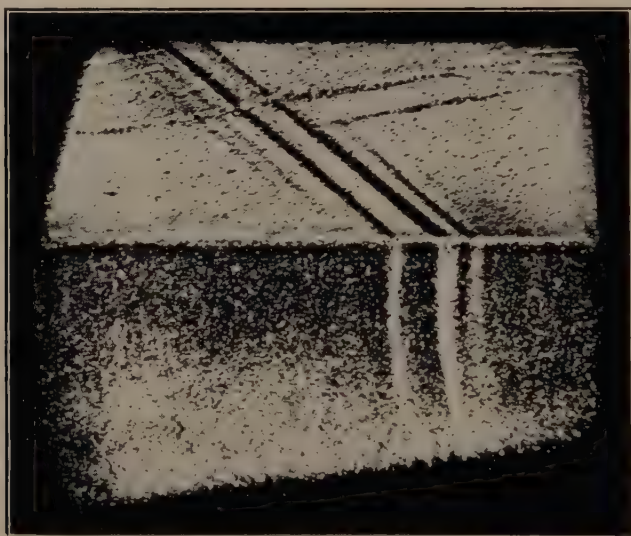


FIG. 9.—DEFORMATION BANDS IN SPECIMEN CUT FROM LARGEST GRAIN OF FIG. 8. $\times 5$.
Compression surface at bottom of picture. Shows two sets of bands.

it is sometimes impossible to decide whether a given grain contains distorted deformation bands or only irregular distortion of a continuous nature, as will be seen from Fig. 8, and one wonders if the mechanism of banding is here working under conditions of strain so inhomogeneous that the crystallographic features are submerged. Another peculiarity of the bands is that they appear to have different widths when seen with different conditions of illumination, which may be explained by assuming a more or less continuous range of orientations across narrow regions at

the boundaries. Grains in which the original compression axis lies in or near a $\{110\}$ plane seldom contain bands after deformation while other orientations often do. This will be seen from the plot of Fig. 10*a*, in which grains of different initial orientations in the blocks of Fig. 1 and Fig. 8 are characterized as either free from bands (open circles), banded (filled circles), or uncertain (partly filled circles).

Deformation of Single Crystals

Single crystals deform in a manner very similar to polycrystalline grains and not in the homogeneous way previous investigators have assumed. Bands and general distortion are common, and when plotted

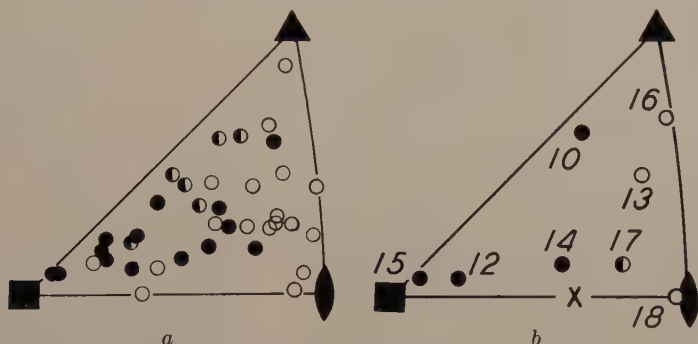


FIG. 10.—DEPENDENCE OF BANDING ON INITIAL ORIENTATION.

(*a*) Individual grains in compressed aggregate. Filled circles indicate initial orientations of grains that subsequently formed deformation bands; open circles indicate those that did not; partly filled circles, those that deformed irregularly but are uncertain as to bands. (*b*) Same as *a* for single crystals. Cross indicates initial orientation of single crystal compressed with special care and used for Figs. 11, 12 and 13.

as in Fig. 10*b* the dependence of banding on orientation is found to be similar to that in polycrystals (Fig. 10*a*). The single crystals were cut in rectangular form, reduced in thickness 50 to 85 per cent by compression between lubricated plates in two to four steps, then compression-rolled to 93 to 97 per cent in eight to ten passes, the final thickness being 0.008 to 0.015 in. Crystal No. 10 was found to have a texture quite like the polycrystalline texture of Fig. 3, as shown by a series of reflection photographs with cobalt radiation; transmission Laue patterns showed, however, that instead of a complete fibering around the axis at any given point in the crystal, there is a scatter about only one or two orientations. Only crystals 13, 16 and 18, which had a $\{110\}$ plane in the compression axis, gave X-ray transmission patterns without a wide scatter, thus confirming the data of Fig. 10*b* based on the appearance of the etched crystals.

To eliminate the possibility that the noncircular initial shape of the crystals or the technique of compression was responsible for the heterogeneous behavior, a crystal whose initial orientation is indicated in

Fig. 10*b* by a cross was prepared with great care in the form of a circular cylinder 0.338 in. in diameter and 0.076 in. thick, with surfaces ground on successively finer emery paper down to 000, with several intermediate etchings. It was compressed between polished steel plates in 25 approximately equal steps, with petroleum jelly applied at each step, to a reduction of 28 per cent. Straight bands of low contrast extending through the disk were clearly visible when the specimen was etched; a photograph is reproduced in Fig. 11. Analysis showed that the bands were parallel to (010) planes, and the orientation difference across a band boundary was 3° (Fig. 12), thus proving that they were deformation bands rather

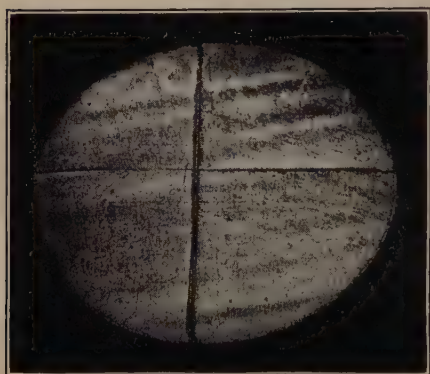


FIG. 11.

FIG. 11.—DEFORMATION BANDS IN SINGLE CRYSTAL. $\times 4.5$.

Compressed 28 per cent with 25 lubrication steps. Bands lie about 10° from the longer of the two scribed lines and are on (100) planes.

FIG. 12.—ORIENTATION RELATIONSHIPS IN COMPRESSED CRYSTAL OF FIG. 11.

Open circle indicates initial orientation, filled circles connected by full line indicate orientations of bands after 28 per cent compression; filled circles connected by dotted line indicate orientations of bands after 50 per cent compression. Orientations in bands are not in relationship for mechanical twins.

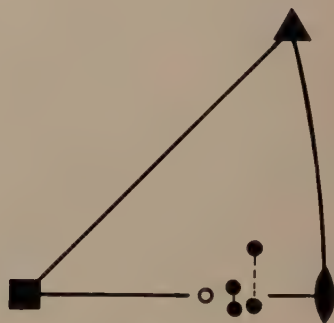


FIG. 12.

than mechanical twins. The disk was repolished and compressed 22 per cent further in 15 steps—a total of 50 per cent. The bands were very slightly curved, and there was a definite orientation variation within each band. The mean orientation difference between adjacent bands had increased to 8° (see Fig. 12), giving a more contrasty appearance than before. For both compressions the two orientations have the [010] axis in common; that is, the pole of the plane of the bands. It might be noted that the rotations are not those that would have occurred if the slip in each band were on one of the two slip planes of highest resolved shear stress (as has been proposed by Elam^{15,16} for a banded structure in aluminum crystals elongated in tension), for this would cause rotations along great circles through the initial orientation and the two closest [111] poles.

A Laue photograph of the crystal after 28 per cent compression shows intense asterism (Fig. 13) indicating a continuous range of orientations of about 3° with the majority of the fragments near the ends of the range.

Taylor and Farren⁸ observed regions of "extraordinary distortion" in some of their compressed aluminum crystals but attributed them to disturbances at the edges of the disks and disregarded them; in a later paper Taylor⁴ found X-ray evidence of a range of orientation amounting to 9° in one of these crystals, but again he disregarded the possibility that deformation bands caused it and attributed his results to the rotation of tiny fragments of elastic material at the ends of cracks or areas of slipping. The direction of the rotation was "the same as that which might be expected if the detached portions of the crystal acted as rollers between slip planes, but it is very much less than would be necessary if they actually played the part of rollers."⁴ Yamaguchi¹⁷ found asterism in the extension of aluminum crystals, which he interpreted similarly, and Burgers and Louwerse⁵ did the same in compressed aluminum, finding asterism corresponding to orientation ranges of 10° to 20° . As these conclusions have been made the bases of theories on hardening and recrystallization, it is worth while to point out that they have already been questioned by one of the authors¹²



FIG. 13.—TRANSMISSION LAUE PHOTOGRAPH OF COMPRESSED CRYSTAL OF FIG. 11.

Tungsten radiation. Asterism is attributed to macroscopic bands and not to local distortion at slip planes.

and are now shown to be unwarranted by the evidence presented in Figs. 11, 12 and 13 for distortion on a macroscopic scale.

DISCUSSION OF RESULTS

It is scarcely to be expected that theories designed to explain a simple [110] compression texture could also explain the range of orientations observed in this research; furthermore, many of them have been based on invalid assumptions regarding the number of slip planes that must operate, as Taylor has pointed out.⁷ In the most recent theory,⁷ Taylor calculates that in grains of polycrystalline aluminum during deformation five slip systems must operate in order to produce the required change in shape of the grains: these are the ones for which the total work of deformation is least. The resulting rotations of the compression axis with respect to the lattice are in the directions indicated by the arrows in Fig. 6, the amount of rotation for a 3 per cent compression being indicated (approximately) by the lengths of the arrows in the figure. In many orientations the rotations are indeterminate and may lie anywhere within a considerable range because two sets of five slip systems can

produce the deformation with an equal expenditure of energy.* When Fig. 6 is compared with the observed mean rotations in Fig. 5, it is found that about half the grains rotate as predicted by the theory, about one-third definitely do not, and the rest are doubtful.

It appears possible to explain the discrepancies between Figs. 5 and 6 and to understand the nature of the deformation texture as follows: The calculations on which Fig. 6 is based were made on the assumption that each grain suffers the same strain as the aggregate, which is not actually true. There are nonuniform constraints on all sides of each grain affecting its strain. If it were possible to choose an effective compression axis that would deviate from the axis of externally applied force but would describe the strain within individual grains or fragments, one could hope to make suitable modifications of Fig. 6 to cover the actual case; unfortunately this does not appear to be possible. The strain in individual grain fragments must, in general, require three unequal principal strains for its specification, which means that the sets of slip systems would be different from those chosen in Fig. 6 where two principal strains are assumed equal.

Owing to the irregular inhomogeneous strain within the aggregate, no theory can succeed in predicting rotations of individual grains without taking into account an almost infinite number of variables. Attention must be directed instead toward a statistical theory that will explain the general trends and the dynamic equilibrium of the deformation texture. Now if we consider the general trends in Fig. 6, rotation away from [111] should be definite and away from [100] should be somewhat less so. For all other orientations—those forming a wide band through the center of the triangle—the path that would be followed by a fragment is indeterminate, and it is just these orientations that exist in the compression texture. We may visualize a crystalline fragment entering this area of the triangle and wandering around, subjected to rather slight forces tending to rotate it predominantly downward and to the right toward [110] and other forces operating in continually changing directions tending to produce a random distribution of orientations. A great number of fragments simultaneously subjected to similar conditions would create a distribution of orientations that is not unlike the distribution of particles in a gravitational field, as in Perrin's experiment. It is con-

* One of the most difficult tasks of a theory of the deformation textures of cubic metals is to explain the different textures of different metals of the same space lattice. Taylor's theory for aluminum, for example, properly predicts the tension texture of the face-centered cubic metals copper, silver and gold, but not aluminum itself, which alone has only a [111] fiber texture without any [100] added. Compression textures of the face-centered metals also differ. Taylor's theory becomes unwieldy when applied to iron, where 48 slip systems operate, for there are 1,712,304 ways of choosing 5 slip systems from the 48.

ceivable that one might even attack the problem advantageously from a standpoint analogous to a Boltzman distribution among different energy states.

The similarity between the orientation ranges of compressed single crystals and polycrystalline grains is readily accounted for by the occurrence of bands or other more irregular fragmentation, which would produce constraints within the single crystals somewhat similar to the constraints encountered by a grain of an aggregate.

SUMMARY

1. The compression texture of polycrystalline aluminum is only roughly approximated by the usual statement that $[110]$ is parallel to the axis of compression; half of the material is more than 10° from this orientation, regardless of the amount of compression. All orientations are found except those having $[111]$ within 20° of the axis, although the amount having $[100]$ within 15° of the axis of compression is very small. This was determined by both X-ray and optical goniometer measurements in the interior of specimens.

2. Individual grains of an aluminum compression specimen do not rotate as units but become distorted with a range of orientation increasing with the deformation. Typical grains spread up to 7° to 10° at 10 per cent reduction in thickness, two or three times this at 30 per cent, and four or five times this at 60 per cent. Grains of identical orientation rotate and spread in different directions, owing to the effect of surrounding grains.

3. The faces of compression specimens that were in contact with each other were roughened by deformation, as a result of inhomogeneous flow. Every grain flows in a manner dictated by its interaction with neighboring material, in which there is an ever changing state of flow.

4. The deformation texture is not a set of stable orientations retained by crystalline fragments when once reached by them, but it is a large range of orientations within which the fragments are constantly moving during deformation. A statistical equilibrium is established between the rotation of the axis of compression away from $[\bar{1}11]$ and $[001]$ directions toward the (100) planes and the $[011]$ direction, balanced against the random rotations caused by the flow in the neighboring material.

5. G. I. Taylor's theory predicts the direction of rotation correctly for one-half or two-thirds of the grains, incorrectly for the others. The deficiency can be ascribed to the inhomogeneity in flow which was not considered in the theory. When this is considered, the observed texture and the predominant trends of lattice rotations for aluminum can be understood, although only statistically; no theory is capable of treating individual grains accurately.

6. Many grains develop bands. The orientation difference across the boundaries of a band when first observed is only a few degrees about a common [100] axis but increases with deformation. The bands, therefore, are similar in type to the deformation bands of iron and are not twins. The boundaries frequently follow cube planes but become curved at higher deformations. Single crystals and grains in which the direction of compression lies in or near the (110) plane seldom form bands; grains of other orientations often do.

7. Deformation bands occur in single crystals even when extreme care is used to deform them homogeneously and they give rise to asterism in Laue photographs like that previously ascribed by Taylor, Yamaguchi, and Burgers to distortions localized at slip planes.

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DISCUSSION

(*W. L. Fink presiding*)

C. H. SAMANS,* State College, Pa.—Is “fragmentation” affected by the type of single crystal used; i.e., whether made by the process of strain annealing or slow cooling from the melt?

It seems unfortunate that the names “deformation bands” and “deformation lines” have been used in the literature sometimes indiscriminately in discussing two quite dissimilar phenomena. Some of my work on cold-rolled single crystals of alpha brass, published about five years ago, seems to have been repeatedly misinterpreted because of this confusion. In one photomicrograph in particular both well marked, broad deformation bands and very fine, dark-etching deformation lines were present. I gave apparently good X-ray proof of the identity of the deformation lines as mechanical twins. The broad bands, which were not discussed, are apparently identical with the bands found by the authors in aluminum, and are entirely separate and distinct from the narrow lines of deformation and should not be confused with them. The reasons advanced for calling the lines mechanical twins were based entirely upon the impossibility of explaining in any other manner the spots found on our X-ray films.

What is the authors’ explanation of the mechanism of formation of their deformation bands? There would appear to be three possible methods of accounting for them. They may be caused by inequalities of deformation in different parts of the specimens, perhaps by inhomogeneity of some kind; they could result from a competition of slip systems or from different slip systems, of two combinations equally stressed, for example, acting in different bands of the crystals; or they might conceivably be formed by a more or less regular process of shear along cube planes instead of octahedral planes. The fact that they are not found in crystals whose surface is near a dodecahedral pole seems to indicate that shear stress alone is not the controlling factor, because it would be under these conditions of orientation that the shear stress on cube planes would seem to tend toward a maximum because of their 45° inclination to the compression axis. On the other hand, their apparent initial parallelism to cube planes also seems puzzling. In work with brass, we found bands parallel to cube planes, but only when a cube plane was initially parallel to the rolling surface. All our specimens were not examined microscopically, however, and it is possible that additional work will reveal a more frequent occurrence of this type of band. Where they did occur the bands seemed to be formed by the second method mentioned above. A reasonably good correlation with the type of deformation that would be expected to result from the action of different possible slip systems was nearly always found.

C. S. BARRETT (authors’ reply).—If I have added to the confusion about deformation bands and lines, I apologize. It may have been because of the absence of photomicrographs in the reprint of Samans’ paper that I studied. Dr. Samans’ concise and clear statement of the types of strain markings in brass is welcome. There may be some questions, however, as to whether the microstructure is always as simple as he thinks. Dr. Brick discusses it at length in a recent paper, with less positive statements about the identity of the various markings. Until proved otherwise in any given case we must consider that the microstructure of a deformed metal might show deformation twins, macroscopic deformation bands, microscopic deformation bands, irregular variations of orientation, or clusters of slip lines.

We believe that the bands form as a result of the operation of different sets of slip systems in different band-shaped regions, and occur when the work of deformation is less for inhomogeneous deformation of the banded type than for homogeneous deformation. We have no more quantitative theory that would serve to predict the crystallographic features of the bands.

* Assistant Professor of Metallurgy, Pennsylvania State College.

Recrystallization Texture of Aluminum after Compression

BY CHARLES S. BARRETT,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

RECRYSTALLIZATION textures—the orientations of grains after recrystallization—have been studied extensively not only because of their metallurgical importance but also because of the information they yield regarding the atomic movements during recrystallization. Recrystallized grains must possess the same orientations as the submicroscopic nuclei from which they have grown, and thus they offer a direct road by which experimenters can penetrate the submicroscopic realm.

Many perplexing results have come of these studies, but one of the most striking has been the apparent difference in behavior between single crystals and polycrystalline grains. For example, Burgers and Louwerse have shown¹ that when single crystals of aluminum are deformed by compression and are recrystallized (at 600° C.) the new grains appear with orientations that are *different* from the orientations of the deformed crystal in which they grew; but polycrystalline specimens, on the other hand, appear to have a [110] fiber texture both before and after recrystallization and thus to *retain* their texture during recrystallization. This apparent difference between the habits of single crystals and small grains is the subject of the first part of the present research and has been explained by findings reported herein. A similar situation appears to exist for aluminum when elongated or drawn into wires, for single crystals alter their orientation^{2,3} and polycrystalline wires retain their texture^{4,5,6} upon recrystallization after elongation (at least with high-purity aluminum), and it is possible that the explanation found in this paper for compression can be extended to cover elongation and other types of deformation as well.

The second part of this paper deals with the theory of recrystallization textures. In the most successful theory for aluminum recrystallized after compression,¹ much weight is given to the orientation of highly stressed nuclei in the deformed material. Taylor's "local distortions" are assumed to exist along the slip planes where displacement has occurred, consisting of fragments rotated in a specific way with reference to the slip plane and slip direction; namely, about an axis lying in the slip plane perpendicular to the slip direction.^{1,7,8,9}

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¹ References are at the end of the paper.

With our increasing knowledge of the structure of deformed crystals, it has become obvious that this "local distortion" picture of Taylor's has not received adequate experimental proof.¹⁰⁻¹³ In view of its fundamental importance to recrystallization theory a detailed test of it is reported herein. The test seems to disprove definitely the specific type of rotation postulated by Taylor and his followers, and consequently to require revision of the theory of Burgers and Louwerse¹ for recrystallization textures.

TEXTURES OF POLYCRYSTALLINE AGGREGATES

The texture of aluminum after compression is only roughly approximated by the usual statement that it is a fiber texture with $[110]$ parallel

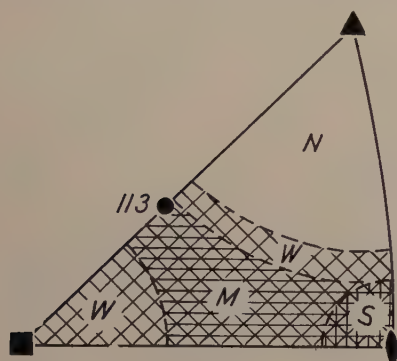


FIG. 1.

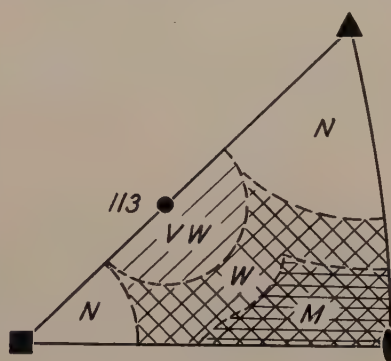


FIG. 2.

FIG. 1.—ORIENTATIONS IN ALUMINUM COMPRESSION-ROLLED 98 PER CENT.

Orientations of compression axis in this and all following triangular plots are indicated by positions within a standard stereographic projection triangle bounded by directions $[100]$, $[111]$, and $[110]$, indicated, respectively, by squares, triangles and ovals. Concentrations of orientations, deduced from intensities of X-ray lines, are labeled strong, medium, weak, very weak, or none (*S*, *M*, *W*, *VW*, *N*).

FIG. 2.—ORIENTATIONS AFTER RECRYSTALLIZATION AT 400° C. IN SPECIMEN OF FIG. 1.

X-ray determination, as in Fig. 1. Only minor differences exist between deformation and recrystallization textures.

to the axis of compression. Half of the material is more than 10° from this orientation, and all orientations are found except those having $[111]$ within about 20° of the axis, although the amount having $[100]$ within 15° of the axis is very small.¹²

The distribution can be represented by a pole figure, with the directions of the axes in the various fragments of the deformed material plotted as points in a unit triangle of a standard stereographic projection. Fig. 1 is a pole figure for fine-grained high-purity aluminum (99.97 per cent Al) compressed to a reduction in thickness of 98 per cent by compression followed by compression-rolling.¹⁰ The figure agrees satisfactorily with those previously published¹² for reductions of 84 and 99.9 per cent, and confirms the statements of the preceding paragraph.

After this specimen was recrystallized by annealing $\frac{1}{2}$ hr. at 400° C.

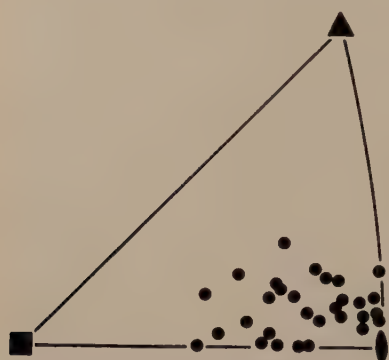


FIG. 3.—ORIENTATIONS AFTER RECRYSTALLIZATION AT 400° C. IN SPECIMEN OF FIG. 1. OPTICAL DETERMINATION.

More than half the grains are 10° or more from $[110]$, as in deformation texture.

unchanged. The same specimen was studied with the aid of an optical

the texture was as shown in Fig. 2. The method of analysis used for Figs. 1 and 2 consisted of setting the specimen at angles suitable for reflecting X-rays ($\text{CoK}\alpha$ and $\text{K}\beta$) from (100) , (110) , and (113) planes lying in or near the surface. After the films were read, arcs were drawn around the corresponding poles of the stereographic triangle to show the range of orientations present.

Figs. 1 and 2 show that the deformation and recrystallization textures are approximately the same. There appears to be a slight reduction in intensity near $[100]$, $[110]$, and $[113]$, but the general features remain



FIG. 4.—ALUMINUM DISKS CONTAINING TWO TO FOUR GRAINS COMPRESSED 75 PER CENT. Actual size. Etching to develop cubic etch pits reveals deformation bands and wavy irregularities.

goniometer, using the reflection of light from cubic etch pits,¹² with the results shown in the pole figure of Fig. 3. Again the same general

features are found: half the material is 10° or more from the $[110]$ position, as it was in an optical study of aluminum compressed 84 per cent (ref. 13, Fig. 2), but areas near $[100]$, $[111]$ and the hypotenuse of the triangle are vacant.

The textures for large grains of aluminum (99.96 per cent pure) were also studied and were similar to the fine-grained textures. Disks about 0.15 in. thick and 0.75 in. in diameter containing 2 to 4 grains each were compressed between polished and greased plates to a reduction of 75 per cent, using 6 to 8 intermediate greasings to lessen the friction at the plates. Fig. 4 shows their appearance when etched with a mixture of 9, 3, 2, and 5 parts, respectively, of HCl , HNO_3 , HF , and H_2O to develop

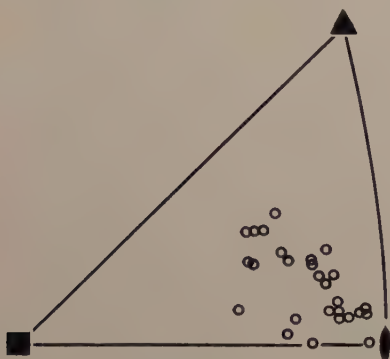


FIG. 5.

FIG. 5.—ORIENTATIONS IN DISKS OF FIG. 4 AFTER 75 PER CENT COMPRESSION. Optical determination at 27 areas on 5 grains.

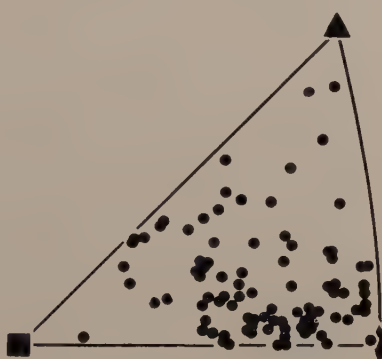


FIG. 6.

FIG. 6.—ORIENTATIONS AFTER RECRYSTALLIZATION AT 400° TO 440° C. IN DISKS OF FIG. 4.

Optical determination in the same areas used for Fig. 5. Similar to deformation texture, with wider scatter.

cubic etch pits. Deformation bands¹² are prominent, as well as wavy irregularities of larger dimensions. An optical goniometer determination of the orientation of 27 small areas in five of these grains gave the deformation texture of Fig. 5. These same areas gave the recrystallization texture of Fig. 6 after annealing a few minutes at 400° to 440° C., indicating somewhat increased scatter but similar trends.

It is clear that the recrystallization texture of a polycrystalline aggregate is similar in type and differs only in details from the deformation texture, and in some cases the difference is scarcely more than experimental error. This is a statistical result, however, and is not true for individual areas of grains, as is shown in the following section.

TEXTURES OF INDIVIDUAL CRYSTALS

The simplest experiments prove that the orientation of a small region in a deformed grain is not retained upon recrystallization. One proof

is furnished by Fig. 7, which shows a portion of one of the large grains of Fig. 4 after partial recrystallization. When light is directed at the specimen so as to reflect brightly from the cubic etch pits of the strained material, as in Fig. 7*a*, all the recrystallized grains appear dark and show strikingly that their orientations are different. When the light is shifted to a new position, as in Fig. 7*b*, their varying degrees of darkness prove that they not only differ from the matrix but differ from each other—

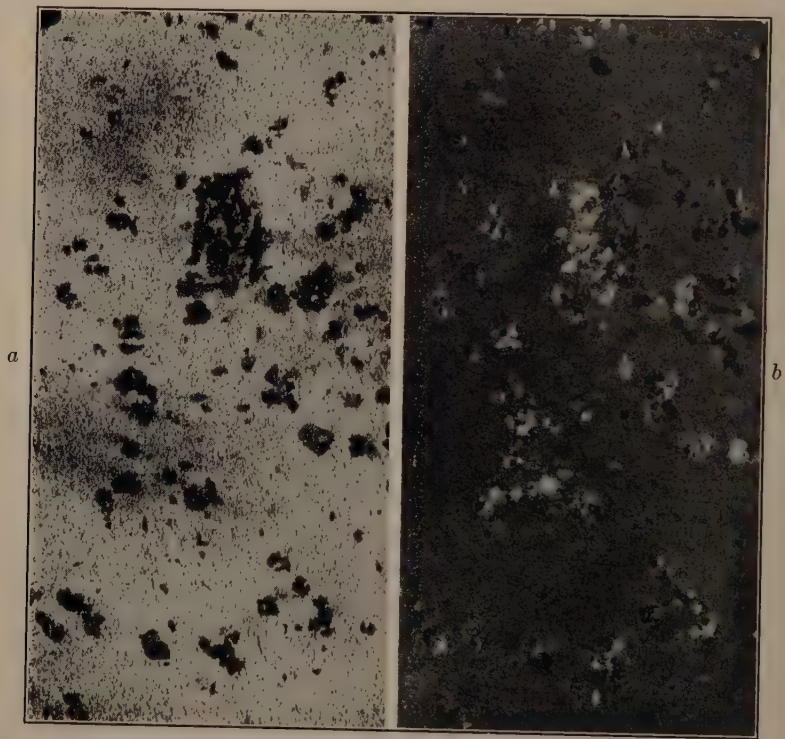


FIG. 7.—PARTLY RECRYSTALLIZED GRAIN SHOWING NEW ORIENTATIONS. $\times 6$. Specimen D, Fig. 4, after 400° C. anneal and cubic-pit etching; (a) light directed to show matrix white, recrystallized grains dark; (b) light directed to show that recrystallized grains occur in groups of different orientations.

although there are some groups of closely similar orientation. The region shown in these photographs was chosen for illustration because of the approximately uniform orientation of the matrix (it was the upper central portion of the right-hand specimen of Fig. 4).

A similar shifting occurs in banded areas, although it is more difficult to recognize there, owing to the considerable range of orientations within each band, and the small widths of the bands. In Fig. 8, two views are reproduced of a banded grain that has been cut in two. The light source was shifted about 10° between the two exposures. One half was recrystallized, re-etched, and replaced in its former position. Light streaks in

the strained half correspond with dark streaks in the recrystallized half more often than not, again indicating new orientations in the recrystallized material, yet orientations that are somehow related to the deformation bands of the strained material, since they also form bands.

Additional proof was obtained by X-ray diffraction. Small-grained compression specimens were mounted in a special holder and transmission Laue photographs prepared. After recrystallization at 400° to 460° C.,

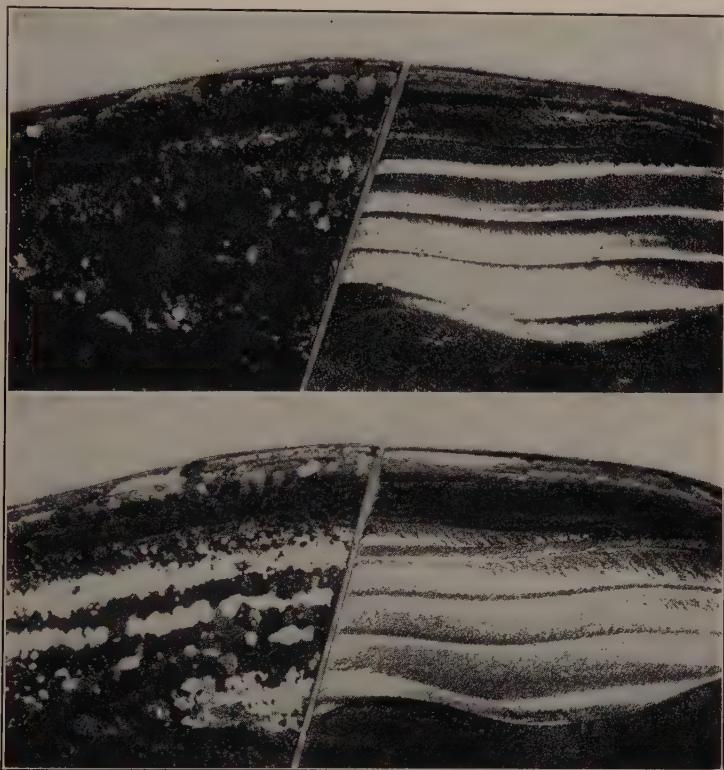


FIG. 8.—DEFORMATION BANDS BEFORE AND AFTER RECRYSTALLIZATION. $\times 6$.

Specimen B, Fig. 4, with half to the left of the cut recrystallized at 440° C. and re-etched. New grains take new orientations that are related to the deformation bands. Light source shifted about 10° between top and bottom pictures.

Laue patterns of exactly the same spots were prepared, with the specimens held in positions identical with the former. While the recrystallized grains often yielded groups of spots, these groups were usually unrelated to the position of the asterism streaks from the deformed material, showing that the recrystallized grains had new orientations. The lack of agreement between the streaks and the spot-clusters in such experiments is easily seen when the X-ray films are superimposed, as in Fig. 9. This type of experiment often gave an inconclusive result because of the many broad streaks from the deformation texture, but enough decisive cases

like Fig. 9 were obtained to establish the principle for both fine-grained and coarse-grained aluminum of high purity and for a wide range of reductions.

A detailed investigation of the orientation relationships was carried out with the optical goniometer, using marked areas on the etched surfaces of deformed and recrystallized grains. A number of the deformation bands in Fig. 8 were analyzed by determining the predominant orientation in a single band and the orientation of the one or two principal groups of recrystallized grains that appeared to have grown within it.

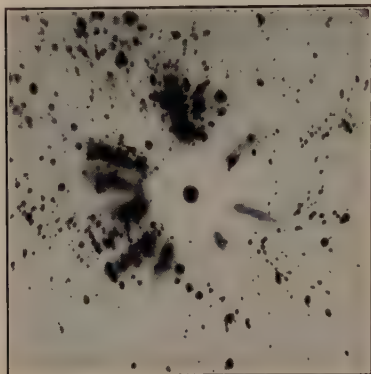


FIG. 9.

FIG. 9.—LAUE PHOTOGRAPHS BEFORE AND AFTER RECRYSTALLIZATION, SUPERIMPOSED. Lack of coincidence between streaks and spot clusters furnishes X-ray proof of new orientations in fine-grained material.

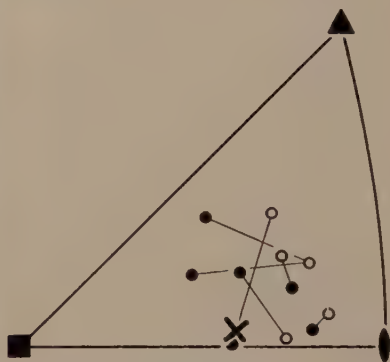


FIG. 10.

FIG. 10.—ORIENTATIONS OF INDIVIDUAL AREAS BEFORE AND AFTER RECRYSTALLIZATION.

Optical determinations in individual bands of Fig. 8. Initial orientation indicated by a cross, deformed by open circles and recrystallized by black circles. Every area altered its orientation.

Both measurements were made as close together as possible to minimize orientation variations along the band. The results are plotted in Fig. 10. The initial orientation is shown by the cross, the orientations after deformation by the open circles, and the orientations after recrystallization by the black dots. All orientations are consistent with the polycrystalline textures discussed in the preceding section, yet in every case the orientation has shifted, as indicated by the lines connecting corresponding deformed and recrystallized orientations.

A large number of similar determinations were made on large-grained material and on single crystals, with similar results. Out of more than 100 recrystallized grains measured in the specimens of Fig. 4, less than 2 per cent appeared to have even approximately the orientation of the matrix in which they grew. This behavior seems to be characteristic of all degrees of deformation, for other experiments with compressions of 4, 21, 66, 82, and 95 per cent gave analogous results.

Stereographic projections in which all three poles are plotted directly as measured in the optical goniometer show the orientations in full detail (though the textures are not seen as readily as in the triangular plots used in the preceding section, where the pole of the compression plane is plotted in proper relation to the standard orientation). The banded grain in the specimen at the bottom of Fig. 4 is plotted in detail in Fig. 11, and the unbanded one in Fig. 12. These circular plots and all other circular plots in the paper are made with the axis of compression at the center of the circle and the plane of compression in the plane of projection. The spread

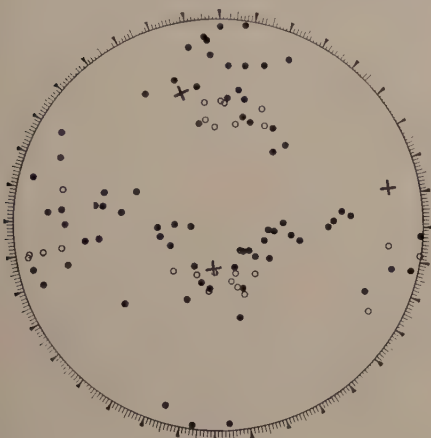


FIG. 11.

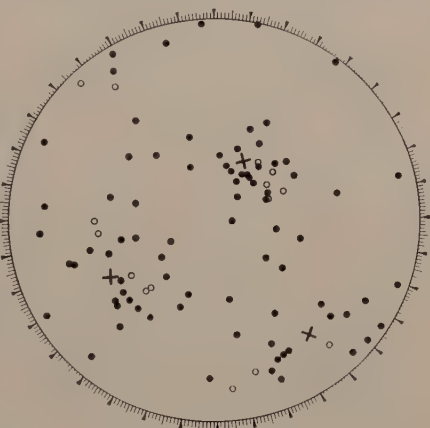


FIG. 12.

FIG. 11.—ORIENTATIONS IN A GRAIN BEFORE AND AFTER RECRYSTALLIZATION.

This and following circular plots show all three cube poles of individual regions or grains with compression plane as plane of stereographic projection. Specimen C, Fig. 4, banded grain; initial orientation, cross; deformed, open circles; recrystallized at 440°C ., black circles.

FIG. 12.—ORIENTATIONS IN A GRAIN BEFORE AND AFTER RECRYSTALLIZATION.

Unbanded grain of specimen C, notation as in Fig. 11. Orientations of individual areas were altered by recrystallization; wide ranges of both deformed and recrystallized orientations.

in orientation of the deformed material (open circles) hides any tendency of the recrystallized grains (dots) to fall into clusters.

In several grains and single crystals, however, there was a smaller range of orientation in the deformed material, and groups of recrystallized grain orientations were clearly seen (such as the group appearing white in Fig. 7b.). Fig. 13 is an example of this. The deformed material had a mean orientation indicated by the black squares, and the recrystallized grains fell into four groups. The three cube poles of each group are numbered 1 to 4 in the figure. This grouping is very similar to the grouping that was found in an X-ray pole figure of a single crystal by Burgers and Louwerse.¹ The grain plotted in Fig. 13 was one having the axis of compression initially 5° from $[110]$ and thus developed no deformation bands.¹² It was in a coarse-grained specimen compressed 66 per

cent. The initial orientation differed considerably from that of Burgers and Louwerse but the amount of reduction was similar.

Another single crystal, which had its axis 2° from $[110]$ and 43° from $[100]$ and deformed into a $[110]$ texture with 94 per cent compression-rolling, was found to recrystallize into a less pronounced texture when held 5 min. at 580° C. Insufficient data were obtained to determine the tendencies toward grouping, but it was evident that both deformation and recrystallization textures were consistent with the polycrystalline texture.

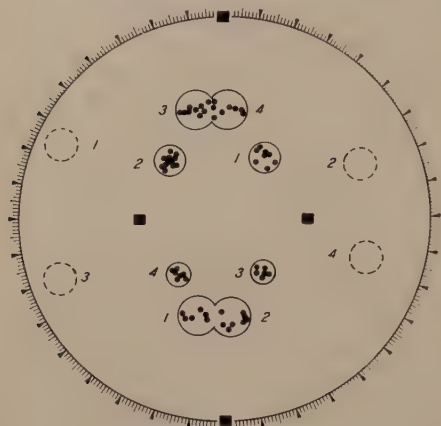


FIG. 13.—RECRYSTALLIZED GRAINS OCCURRING IN GROUPS.

One grain of a coarse-grained specimen, compressed 66 per cent and recrystallized at 375° C. Mean orientation of cube poles before recrystallization shown by squares; after recrystallization by dots in four groups.

determined. Fig. 14 is the X-ray pole figure of the deformed crystal, showing a concentration at $[110]$ and a wide scatter toward $[100]$, and

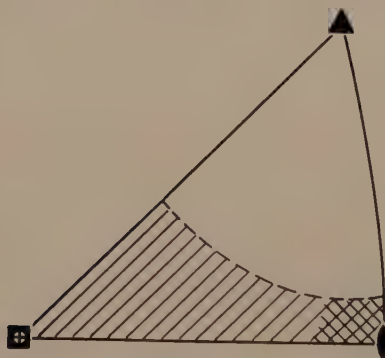


FIG. 14.

FIG. 14.—ORIENTATIONS IN A SINGLE CRYSTAL AFTER 97 PER CENT COMPRESSION-ROLLING.

There is a strong concentration at $[110]$ but a wide range of low intensity.

FIG. 15.—ORIENTATIONS IN CRYSTAL OF FIG. 14 AFTER RECRYSTALLIZATION AT 450° C. An unusually small range of orientations.

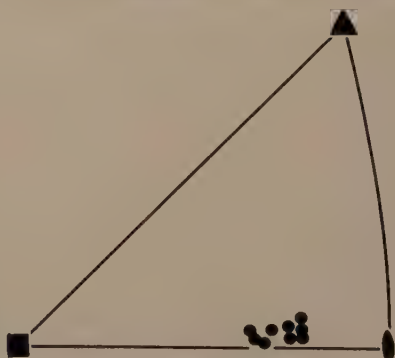


FIG. 15.

Fig. 15 is the optical pole figure after recrystallization. More complete optical data for this crystal is shown in Fig. 16, where the groups of cube poles are indicated by sets of circles numbered 1 to 9.

An attempt was made to obtain an ideal recrystallization texture by choosing a crystal with an orientation such that deformation bands would not form and compressing it with great care to reduce friction and to

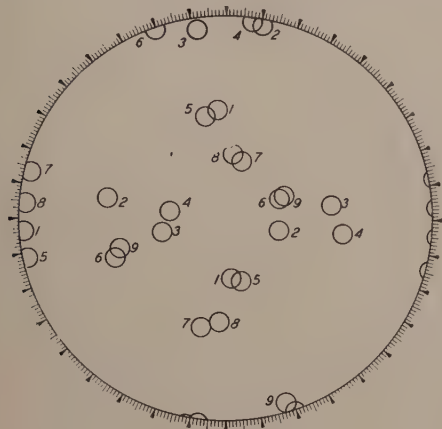


FIG. 16.

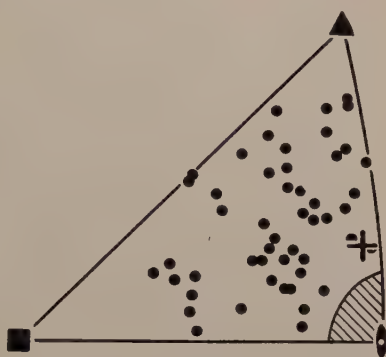


FIG. 17.

FIG. 16.—DATA OF FIG. 15 PLOTTED TO SHOW GROUPING OF CUBE POLES.

FIG. 17.—SINGLE-CRYSTAL DISK COMPRESSED 69 PER CENT WITH SPECIAL CARE.

Initial orientation (indicated by cross) chosen to prevent deformation bands; deformed orientation in small range (shaded); recrystallization orientations widely scattered (black circles), and, as in other examples, not the result of twinning of strained matrix.

provide homogeneous strain. The initial orientation is shown by the cross in Fig. 17 and the texture after 69 per cent compression is shown by the shaded area, which is derived as a mean of the X-ray pole figure data of Fig. 18. This crystal, initially 0.5 in. in diameter and 0.048 in. thick, was carefully polished and compressed 69 per cent between polished steel plates, which were lubricated 30 times at equal increments of load, and was ground into a right circular cylinder five times during the compression. The technique used appeared to be adequate, for the deformed crystal, after etching, had the appearance of a single crystal and gave Laue patterns of the type shown in Fig. 19, exhibiting unusually sharp spots and streaks corresponding to a very small range of orientation (see Figs. 17 and 18).

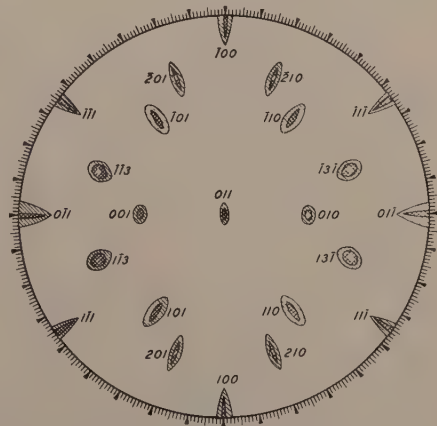


FIG. 18.—POLE FIGURE (X-RAY) OF DEFORMED CRYSTAL OF FIG. 17.

The recrystallization texture developed in this crystal by a 2-min. anneal in a lead bath at 455° C. is shown by the dots in the triangular plot

of Fig. 17, and in detail in the full plot of cube poles in Fig. 20, where the three poles of each of 50 measured grains are indicated by dots numbered



FIG. 19.—LAUE PHOTOGRAPH OF CRYSTAL OF FIG. 17.

Beam normal to specimen; photograph turned to correspond to Figs. 18, 20, 21, 22 and 23. Narrow streaks near center are not in agreement with Taylor theory of "local distortion."

from 1 to 50 and the mean orientation of the deformed crystal by black squares.

The plots show that the recrystallized grains all have orientations not

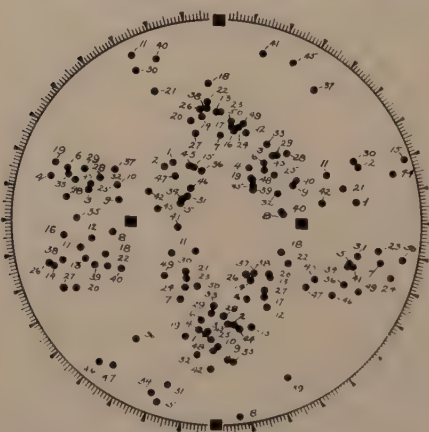


FIG. 20.—ORIENTATION OF 50 RECRYSTALLIZED GRAINS IN CRYSTAL OF FIG. 17.

Mean orientation of deformed crystal indicated by squares, of grains formed by recrystallization at 455° C. by dots numbered from 1 to 50.

present in the deformation texture of the crystal and that they are scattered widely. Half of the grains lie 20° or more from [110]. In spite of the wide scatter, however, the texture is not random but tends to show groupings somewhat similar to Fig. 13, avoiding [110], [100] and [111] positions.

The appearance of the specimen after recrystallization (Fig. 21) suggests a Widmanstätten pattern owing to the directions taken by a number of elongated grains. The orientation of Fig. 21 corresponds to that of Figs. 18, 19 and 20; the grains therefore appear frequently to have their

longest and straightest boundaries parallel to (111) planes of the deformed matrix in which they grew. A twin relation between neighboring grains

is sometimes found. Grains 38 and 42, for example, have the matrix (111) plane as a boundary and also as a (111) plane in each. In this connection it might be noted that the two grains of specimen D in Fig. 4 were annealing twins—in this case presumably resulting from the slight tensile strain.

No systematic study was made of the effects of varying the percentage reduction, the annealing temperature, or the schedule of intermediate

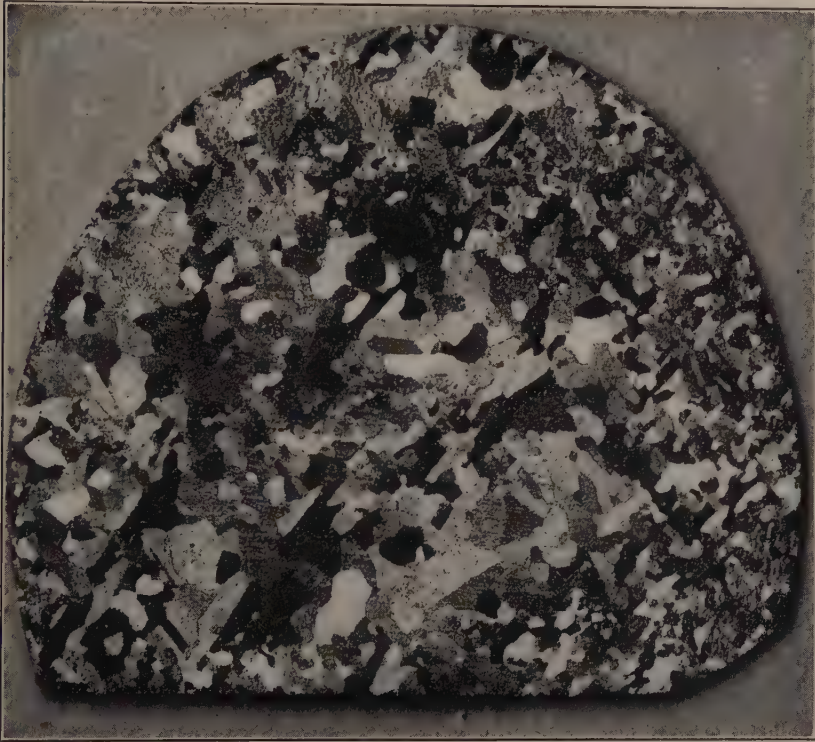


FIG. 21.—APPEARANCE OF CRYSTAL OF FIG. 17 AFTER RECRYSTALLIZATION. $\times 7$.

A Widmanstätten appearance is caused by grain boundaries along (111) planes of deformed crystal, some of which separate annealing twins.

anneals on these textures. It was noted, however, that recrystallized grains were often found with orientations outside the recrystallization texture when the compression was slight (4 and 21 per cent), whereas this occurred less often with reductions of more than 60 per cent. But Fig. 17 proves that sharp deformation textures do not necessarily cause sharp recrystallization textures.

A TEST OF THE "LOCAL DISTORTION" THEORY

The pole figure of the carefully compressed crystal, Fig. 18, was prepared as a critical test of the theory of "local distortion" advanced by

Taylor,⁸ and upheld by Yamaguchi⁹ and by Burgers and Louwerse,¹ and expanded by Burgers and Louwerse into a theory of recrystallization textures.

The crystal was chosen, as already stated, so as to preclude deformation bands, and was compressed with the usual precautions to minimize bend gliding and other inhomogeneities. A pole figure (Fig. 18) was then plotted for a number of important planes, using transmission Laue photograms taken with a molybdenum tube. Heavily shaded areas were located by data from white radiation reflections, the larger lightly shaded areas by data from the more intense $K\alpha$ radiation. The exact limits of



FIG. 22.—ORIENTATIONS PREDICTED BY TAYLOR'S "LOCAL DISTORTION" THEORY FOR CRYSTAL OF FIG. 17.

Rotations of 10° each way from the mean about axes normal to the slip directions in the two highest stressed slip planes. Comparison with Fig. 18 reveals definite discrepancies although the range of orientations is similar.

directions of the arrows, but only within a 2° spread in directions perpendicular to these, so the arrows should closely resemble the pole figure actually observed.

Comparison of Figs. 18 and 22, however, shows serious discrepancies. The (100) and (01 $\bar{1}$) poles at the periphery are clearly different in the two figures. If the theory were correct, Fig. 18 should not have a single sharp point at the inner extremity of these areas, but should have a double point (or, with greater scatter, a blunt end). This would be immediately recognized in the Laue photogram with the beam normal to the sheet, Fig. 19, for it would require the outer ends of the streaks near the central spot of the pattern to be doubled azimuthally, or, if the scatter were too great to permit resolution into two streaks, it should require wide bands instead of sharp streaks. Actually the streaks are almost as sharp as

these are, of course, somewhat dependent on exposure times, for weakly populated regions with overexposures resemble strongly populated regions, and there is also some danger of halation on the films with overexposure. The predictions of the Taylor theory are embodied in the pole figure of Fig. 22. The arrows indicate the movement of the poles that would occur if crystalline fragments rotated as specified in the theory. The lengths of the arrows are made to correspond to a 10° rotation about each of the four "local distortion" axes that lie normal to the slip directions in the two highest stressed slip planes. Taylor⁸ reported finding crystallites throughout a 9° range in the

the geometry of the pinhole system permits, and show no trace of the doubling or widening demanded by the theory.

While the fragment orientations cannot be described by the Taylor theory, it is nevertheless true that in every cubic millimeter of the compressed crystal there is a range of orientations amounting to as much as

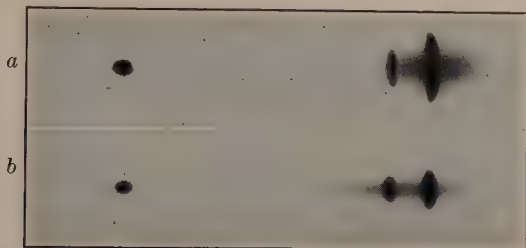


FIG. 23.—(022) REFLECTIONS CORRESPONDING TO CENTRAL SPOT OF FIG. 18.

Spots from direct beam are at left, (022) reflections at right: (a) reflection circle vertical at center, Fig. 18; (b) reflection circle horizontal at center, Fig. 18. Shows that central area of Fig. 18 is elongated vertically.

$\pm 10^\circ$ about several axes. If one attempts to deduce these axes there are at least two important items to consider: (1) All poles at the periphery of Fig. 18 are spread radially almost five times as much as azimuthally, and (2) the central (011) pole is spread about twice as far toward (100) as toward (01 $\bar{1}$). Item 1 can be seen directly by inspection of the radial nature of inner streaks of Fig. 19, and item 2 by Fig. 23, which shows the (022) reflection, with the beam directed so as to register the length of the major and minor axes of the elliptically shaped pole figure areas as azimuthal widths of the two (022) streaks. That there are a number of rotation axes lying in the plane of the compressed specimen is suggested by item 1 and it could be accounted for, in fact, by the collective action of axes at all angles in this plane. This would predict a pole figure like Fig. 24, constructed by rotating $\pm 10^\circ$ about all axes in the plane of the projection. Item 2, however, indicates that there is a greater range of rotation about axes near [01 $\bar{1}$] than about axes near [100]. To attempt a more precise specification of the axes of rotation from these data would be mere speculation.



FIG. 24.—ORIENTATIONS THAT WOULD BE PRODUCED BY ROTATIONS ABOUT ALL AXES IN COMPRESSION PLANE.

Rotations of 10° each way about all axes give approximate agreement with Fig. 18.

DISCUSSION

It is not to be expected that one could derive a sound theory of recrystallization textures from experiments of such limited scope as these, and we shall not attempt to do so. We shall merely criticize some of the prevailing theories and make some general suggestions.

It is probable that the retention of aggregate textures on recrystallization is accompanied by a shift of orientations in individual areas in the case of other metals and other types of strain than those studied here. This is consistent with the fact that most of the compression and elongation textures of metals are believed to be retained by recrystallization, and most of the rolling textures altered. Owing to the lower symmetry of the rolling textures the alterations should be more easily recognized in the aggregate.

Dehlinger's theory¹⁴ of recrystallization textures in aluminum appears to have no merit in view of the results reported herein, for it is based on the assumption that when deformation and recrystallization textures are alike each recrystallized grain has the orientation of the matrix in which it grew. This assumption is invalid for the case of compression, and may well be so for other types of deformation also.

Burgers' theory of strain-hardening and of recrystallization of aluminum* relies heavily upon "local distortions" of the type postulated by Taylor, and Burgers considered that his recrystallization textures in compressed single crystals confirmed the Taylor distortions. Burgers' results on polycrystalline aluminum, which he considered inconsistent with the Taylor theory, were attributed to a more inhomogeneous flow that would not permit the Taylor distortions to develop to an important extent.

The present results, as they do not confirm Taylor's type of distortions, mean that many of Burgers' concepts must be revised. There is now no experimental basis for assuming that small fragments are rotated somewhat like rollers between the slipping surfaces, and that those that have been rotated 50° to 60° are strained enough to act as nuclei for recrystallization. Burgers and Louwerse¹ were not able to find X-ray evidence of fragments in this range, but extrapolated from a range less than one-third of this; thus they did not have experimental proof either of the existence of these rotated nuclei or of their condition of internal stress. The present studies have removed the difference in behavior between single crystals and polycrystalline grains that Burgers attempted to explain.

* See ref. 1, and W. G. Burgers' chapter in Reports of the International Conference on Physics, **2**, Phys. Soc., London, 1935.

If we object that the type of rotations Burgers used are not found in the deformed crystal, we must ask whether the rotations that do exist in the deformed material, or an extension of these, can explain the observed textures, such as Fig. 13, for example. We find that there is at least one set of rotation axes that fulfill this requirement; namely, $[11\bar{1}]$ and $[\bar{1}1\bar{1}]$, which lie normal to the compression axis. Rotations up to 10° each way about these two axes describe the major and minor axes of the pole-figure areas of Fig. 18 reasonably well, and rotations of 45° each way from the deformation texture explain the recrystallization texture of Fig. 13 and of two other grains, not included in the illustrations, that showed well-defined textures similar to this. If these axes alone were operating, however, they would cause a double (022) streak instead of a single one in Fig. 19, corresponding to a cross-shaped (022) area at the center of the pole figure (Fig. 18), which is not observed. It seems hardly likely that these axes will furnish an important clue to the recrystallization mechanism.

The results in this paper are not readily explained on the basis of deformation twins acting as recrystallization nuclei. Twinning of the deformation texture of Fig. 13, for example, will not yield the recrystallization texture of that figure, and the same can be said of the single crystal of Figs. 14, 15, and 16; in Fig. 20 only a few grains have a twin relationship with the deformation texture of Fig. 18. Grains in which there are wide ranges of orientation or narrow deformation bands in the strained matrix are not well suited to a test of this theory (for example, Figs. 10, 11, 12). Theories based on variations of internal stress within differently oriented nuclei¹⁴ would be susceptible of proof only if X-ray reflections from the nuclei could be observed.

At the moment it appears that a theory could be based on the relative rates of growth of differently oriented nuclei into the deformation texture material. The shifting of atoms from the strained matrix to the new grain might be imagined to proceed slowly if the new grain had the orientation of the matrix, and fastest if the orientation differed a certain way. Or one might postulate that the important concept was the stability of the nuclei in different orientations. In either case the theory becomes one in which the strained matrix orientation takes a prominent place, as unquestionably it should.

SUMMARY

1. The deformation and recrystallization textures of polycrystalline high-purity aluminum after compression are of the same type. They consist of a wide range including all orientations except those having $[111]$ near the axis of compression, although there are but few fragments having $[100]$ near the axis. The mean orientation is $[110]$.

2. Each recrystallized grain has an orientation different from that predominating in the matrix in which it forms. Exceptions to this rule are very rare, either with grains or single crystals.

3. Individual areas alter their orientation without complete loss of texture of the aggregate, owing to a tendency of the recrystallized grains to avoid orientations having $[111]$ or $[100]$ near the axis of compression.

4. Groups of orientations tend to occur among the recrystallized grains but are not always sharply defined, even when the deformation texture is sharp. Some groupings are like those found in single crystals by Burgers and Louwerse.

5. Traces of the original grains are visible after recrystallization because within each old grain many of the new grains have like orientations.

6. Several instances were found in which the orientation of the recrystallized grains are not accounted for by twinning the deformation texture; this mechanism appears unimportant in the recrystallization of aluminum.

7. Annealing twins occur in aluminum, for pairs of adjacent recrystallized grains have been found bearing a twin relationship to each other, separated by a (111) plane common to both. In one case this was also a (111) plane of the matrix.

8. Deformation bands in the strained material lead to bands of similarly oriented recrystallized grains.

9. A critical test of Taylor's theory of "local distortion" at the surfaces of active slip planes was made on a specimen deforming without deformation bands. While fragments were found distributed throughout a range of 10° from the mean orientation, the spread was not in the directions required by the theory.

10. These results invalidate or require modification of several theories of recrystallization textures, notably those relying on Taylor's "local distortions" and those attributing the retention of the polycrystalline texture to a retention of orientation in individual areas.

ACKNOWLEDGMENT

The author acknowledges with pleasure the skillful work of his assistant, Mr. L. H. Levenson, in preparing specimens and in determining orientations in the optical goniometer.

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DISCUSSION

(Cyril Stanley Smith presiding)

R. M. BRICK,* New Haven, Conn.—In one set of tests, the author states that a crystal was chosen with an orientation such that deformation bands would not form upon compression. It appears that the actual orientation was not a stable one in relation to the usual deformation texture and the crystal must have rotated as a unit to the final texture position rather than by division into bands. This result is not in accordance with our preconceived idea based on the author's previous work. The questions naturally arise as to what range of initial orientations may be deformed without banding and whether the range includes the so-called stable orientation; i.e., one unchanged by the deformation.

The crystal showed annealing twins, confirming the belief that in this regard aluminum differs from other face-centered cubic metals only in degree and not in kind. Since other evidence has indicated that annealing twins in brass and bronze grow from strain markings, is it possible that this specific aluminum crystal, while lacking wide deformation bands, may have shown some scattered strain markings?

The author's clear analysis of carefully obtained experimental data makes it evident that the present most widely accepted theory of recrystallization textures is inadequate. It may be suggested that no general theory in this field need apply for recognition unless it conforms to evidence of the type presented here when such evidence becomes available for most of the common metals. At the same time, this work reveals the need for constructive data on the question of what parts of the deformed structure constitute the nuclei that are most favored during subsequent growth to form the recrystallized aggregate.

W. G. BURGERS,† Delft, The Netherlands.—Dr. Barrett's paper deals with certain views put forward in a paper by myself and P. C. Louwerse,¹⁵ which are summarized in

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† Laboratory of Physical Chemistry, Technische Hoogeschool.

¹⁵ W. G. Burgers and P. C. Louwerse: *Ztsch. Physik* (1931) **67**, 605.

a paper read for the International Conference on Physics held in London in 1934.¹⁶ Briefly, the views expressed in the two papers mentioned regarding the deformation and recrystallization of aluminum single crystals and polycrystalline test pieces are as follows:

1. The fact that homogeneously compressed single crystals (as deduced from their macroscopical change in form) showed that Laue asterism was considered to be an indication that the glide-lamellae were "locally" curved.

2. From the direction of the striae it was deduced that the "axis of curvature" lies in the plane of the lamellae, perpendicular to the direction of gliding.

These views had already been put forward by Taylor and by Yamaguchi for crystals that had undergone gliding along one set of glide planes, but was extended as a result of our experiments to cases where gliding had taken place along several sets of planes.

3. "Local curvatures" had to be assumed to occur along *every* set of planes. The possible occurrence of lattice parts, *rotated about several axes in turn*, seemed probable and arguments in its favor were advanced.

4. The occurrence of the "local curvatures" mentioned was considered to be confirmed by the preference orientations of the crystallites, formed after recrystallization of the deformed crystals: these orientations could roughly be deduced from that of the main body of the deformed crystal by rotations about the axes mentioned above, the necessary rotations, however, being much larger (about 20° to 60° instead of about 10° to 20° in the not-recrystallized state). This result could be understood by assuming that as "nuclei" of the new crystallites the parts of the local curvatures served in which the distortion-gradient is severest are the parts where the rotation is greatest. The fact that as many groups of new crystallites were found as glidings had taken place during the deformation was considered to be a confirmation of point 3.

5. The difference in orientation between deformed crystal and recrystallized grains, as set forth in paragraph 4, was *not* observed when recrystallizing deformed polycrystalline (*fine-grained*) test pieces. In order to explain this different behavior, it was assumed that the "local curvatures" in each individual grain of the fine-grained test piece were very small, because the gliding of each grain was hindered to such an extent by its neighbors that the total deformation could be brought about only by many glidings, the amount of slip along each glide system, and thus the local curvature of the lamellae, being small. Large differences in orientation between a "nucleus" and the main body of the glide lamellae could then not be expected.

The first important result of Dr. Barrett's investigation in connection with this subject is the establishment, put forward in particular in a former paper,¹² that on deformation of aluminum crystals often regions of macroscopic dimensions can be discerned (for example, optically) in which the active glide directions are different from those in adjoining regions. These regions, which often are separated by straight lines, are called deformation bands, and must be discriminated from the glide bands or glide lamellae. Such bands can be slightly curved and there is a definite orientation variation within each band (ref. 12, p. 11). It was thus stated (ref. 12, p. 15, also ref. 10) that the orientation differences across these bands are responsible for the broadening of the Laue spots and not the "local curvatures," as assumed in Taylor's and in our theory. However, in the present paper (pages 135 and 137) crystals were deformed without developing deformation bands and yet apparently Laue striae were formed, so that Barrett (p. 141) comes to the conclusion "that in every cubic millimeter of the compressed crystal there is a range of orientations amounting to as much as $\pm 10^\circ$ about several axes." It thus seems to me that with regard to point 1 above this statement removes much of the difference in view held by us and that put forward in

¹⁶ Papers and Discussions, Int. Conf. on Physics, London (1932) 2, 139.

this paper. Although in a deformed crystal the Laue asterism may be due to curvatures over "larger" and to curvatures over "smaller" regions, the latter certainly play a part in the deformation process. (Also, Komar and Mochalow¹³ have suggested that the Laue asterism is due to curvatures over large distances. See, however, in this connection my remark in Chapter V of R. Houwink's *Elasticity, Plasticity and Structure of Matter*, 95. Cambridge, 1937.)

Dr. Barrett concludes from his analysis of the direction of the Laue striae that they cannot be explained on the assumption of axes of curvature as suggested in paragraph 2 above. Instead, it is suggested that they can be accounted for by the collective action of axes lying in the plane of a compressed specimen. This is a point that deserves careful consideration. We set forth in our paper that it is rather difficult to deduce the direction of the axes of curvature from the direction of the Laue striae, as this direction is rather insensitive for a change in orientation of these axes. We therefore relied mainly on the fact that the Laue spot for the plane (112), perpendicular to the axis of curvature assumed by us, remained fairly sharp in the photographs and further based our conclusion on the position of the recrystallized grains (see paragraph 4). The large spreading of the orientations of these crystallites about the assumed directions was suggested by us to be at least partly due to the fact that in the deformed crystals, in which in all cases gliding had taken place about at least four intersecting glide systems, the curvature of the lamellae may be brought about by *combination of rotations* about the various possible axes (Figs. 18 and 19 of our paper in *Ztsch. Physik*). It is not easy to see precisely in how far asterism as observed by Dr. Barrett can be explained in this way. According to the results given in the present paper, one must certainly reckon with the possibility that our former assumptions regarding the directions of the curvatures of the glide lamellae need revision. (I may add, however, that the statement at the bottom of page 141 of this paper, that "there is a greater range of orientation about axes near [110] than about axes near [100]," would make the axes assumed by Dr. Barrett approach those assumed by us, as a close comparison of our papers will show.)

With regard to point 4, Dr. Barrett's and our results agree that the orientations of the new crystals, formed after recrystallization, differ from that of the main part of the lamellae in the compressed crystal; that is, from the deformation texture as revealed in the X-ray photographs. As is especially clear from his Figs. 13 and 20, the orientations found in both researches have much in common. The fact that other orientations are found is not surprising, considering the possibility that other glide systems than those taken into account (so-called "forbidden glide systems") may have played a part in the deformation process. It seems possible that they may be explained along lines similar to those assumed to hold for the other orientations. (It may be noted that the axes of rotation $[11\bar{1}]$ and $[\bar{1}\bar{1}1]$, suggested on page 143, differ by only about 20° from the directions of the axes [112] suggested by us.)

Finally, there is the question, discussed in paragraph 5, of the discrepancy between single crystals and polycrystalline test pieces with regard to the orientation of the new crystallites formed after recrystallization. Dr. Barrett concludes that this discrepancy is only apparent, as he shows that on recrystallizing test pieces consisting of, say, four crystals, the grains formed in each of them after recrystallization are different in orientation from the respective "mother crystal." He shows, moreover, that the same holds for the crystals formed within each individual "deformation band" within a single crystal, as is clear from their appearance after etching. I perfectly agree with this conclusion, which shows itself to some extent also in results obtained by other investigators, for example those by Bohner and Vogel.¹⁷ Our observations, as mentioned before, however, were made on very fine-grained test pieces, and it was

¹⁷ Bohner and Vogel: *Ztsch. Metallkunde* (1932) **24**, 169.

impossible to decide experimentally whether the new nuclei formed in each individual grain nearly coincide with that of the grain itself or whether the orientations are different. If the latter is true, the identity of the texture before and after recrystallization would be only apparent and be due to the fact that the orientation spreading is already relatively large in the deformed test piece and coincides only statistically with that in the recrystallized test piece. This is, if I am not mistaken, the view held by Dr. Barrett and it may be right, and closer to the truth than that suggested by us in paragraph 5. I only wish to point out that I have the impression* that this conclusion is reached by extrapolating the results obtained with fairly coarse-grained test pieces to very fine-grained ones and therefore asks for closer inspection. Meanwhile, it would seem worth while to investigate whether the occurrence often observed when single crystals are being prepared by recrystallization of slightly stretched polycrystalline aluminum wires, of crystals with a [110] direction parallel to the direction of drawing (and moreover, when stretching flat plates, with the (100) plane parallel to the plane of plate¹⁸) can be explained with the aid of the views suggested in this paper.

It is perhaps worth while to mention that the observation that the new grains frequently appear to have their longest and straightest boundaries parallel to (111) planes of the deformed matrix in which they grow (Fig. 21) was also observed in a very striking way in experiments by Kornfeld and Rybalko,¹⁹ in whose paper attention is also drawn to the influence of the relative orientation of nucleus and matrix on the way of growing of the nucleus.

H. E. STAUSS,† Newark, N. J.—To judge from Fig. 21 and the experimental details on page 137, the final grains were as large and even larger than the thickness of the specimens. I wonder whether this has had any influence upon recrystallization or grain growth of the specimens of this or similar experiments. Extensive tests several years ago with thin platinum foil produced baffling results and indicated an influence of specimen thickness upon the final grains. Thin samples soon confine recrystallization and grain growth to two dimensions and to those grains that can best grow in these directions.

G. SACHS,‡ Cleveland, Ohio.—I agree with Dr. Barrett regarding the differentiation of different types of stresses. However, if atomic dimensions are considered the term "stress" becomes rather indefinite. Thus, a condition may exist in cold-deformed metals that can be described in a simple way by saying that the atoms are irregularly displaced by a slight amount from their normal positions, in a similar manner to that of thermal agitation at high temperatures except that the result is permanent. This phenomenon is the only one surviving, of all the numerous geometrical "distortions" possible in crystals, that can still be made responsible for the strain-hardening. However, the reason that this theory still persists may be that surprisingly little work has been done to investigate the X-ray intensities, which are probably closely correlated to this type of distortion.

C. S. BARRETT (author's reply).—In answer to Dr. Brick, the range of orientations that may be deformed without banding has been plotted in a previous paper¹²; the

* I am not certain, however, about Fig. 9 with regard to this point.

¹⁸ *Ztsch. Physik* (1933) **81**, 43.

¹⁹ Kornfeld and Rybalko: *Physikal. Ztsch. Sowjetunion* (1937) **12**, 658.

† Research Physicist and Metallurgist, Baker and Co.

‡ Assistant Professor, Metallurgical Department, Case School of Applied Science.

range includes the so-called stable orientation. The present results are in agreement with the findings of the earlier paper. We agree with Dr. Brick that microscopic studies of strain markings, possible deformation twins, and recrystallization nuclei should be valuable even though some photomicrographs on these subjects are already available in the literature.

The influence of specimen thickness discussed by Mr. Stauss is, of course, not tested in these experiments. It does not follow, however, that if thin sheets show a rate of grain growth different from that of thick sheets there must also be different kinds of orientations in the two cases, or even different rates of nucleation. Since the original recrystallization nuclei are infinitesimal in size compared with the thickness of the sheet, one would surmise that their behavior would be independent of sheet thickness, other things being equal.

In regard to Dr. Burgers' comments, it seems important to emphasize that asterism in Laue photograms may arise from various causes, none of which can be disregarded if the local distortion theory is to be tested. In the paper of reference 12 we concluded that other causes had been disregarded in previous studies; for example, macroscopic deformation bands and the variation of orientation across these bands. The technique used in the present investigation seems to have eliminated this cause, by eliminating the bands themselves, but asterism could still arise from either a misalignment of fragments throughout the crystal or from the local regions postulated discussed by Dr. Burgers. A direct test to decide whether one or both of these causes is operating is extremely difficult, and I am not convinced of the value of the indirect tests favored by Dr. Burgers (implications from the deformation and recrystallization textures of single crystals). In this paper we find, to be sure, a deformation texture (Fig. 18) that is inconsistent with the particular axes of local curvature proposed by Taylor, Yamaguchi and Burgers. Yet if a local-curvature enthusiast were to alter his theory and base it on a different set of rotation axes—for example, certain [111] axes—I believe the present experiments could neither prove nor disprove it. Another type of theory that can hardly be proved or disproved is one based on a combination of rotations about several axes, since any orientation whatever, or any range of orientations, can then be embraced by the theory, unless limiting assumptions are made which in themselves are difficult to test.

A cause of asterism that is receiving much attention in recent months is the distortion from thermal agitation.²⁰⁻²² Thermal displacements of atoms produce radial Laue streaks much like Fig. 19 in appearance and add to the difficulty of testing local distortion theories.

Dr. Burgers wonders whether grains of aluminum can be made small enough so that they will cease seeking new orientations upon recrystallization. We can only reply that over the whole of the grain-size range we tested, down to a fraction of a millimeter average diameter, the orientations altered in the way we have described, and this range probably covers the range used in previous investigations and in general commercial practice.

R. F. MEHL, discussion on page 168.

²⁰ A. P. R. Wadlund: *Phys. Rev.* (1938) **53**, 843.

²¹ G. D. Preston: *Proc. Roy. Soc.* (1939) **172**, 116.

²² W. H. Zachariasen: *Phys. Rev.* (1940) **57**, 597.

Plastic Deformation and Recrystallization of Aluminum Single Crystals

By J. A. COLLINS,* JUNIOR MEMBER, AND C. H. MATHEWSON,† MEMBER A.I.M.E.

(New York Meeting, February 1940)

THE process of plastic extension of face-centered cubic single crystal-line rods is so well understood, since the notable studies of Taylor and Elam,¹ that the change in orientation of any crystal by slip and rotation may be predicted from the measured elongation. It is customary to assume a very homogeneous deformation, wherein gliding lamellae are free to rotate so that their slip direction continually approaches the axis of the rod, until a second slip system comes into operation; whereupon conjugate slip proceeds quantitatively to an end adjustment with the [112] direction in the axis of the rod.

This process has been checked in many face-centered cubic materials and readily permits the preparation of specimens that have been subjected to various determinable amounts of shearing action.

It is clearly of interest to study in such measurably strained specimens the development of a recrystallized structure on annealing and if possible detect the source of nuclei from which the new crystals grow. Strain-annealing experiments of this character have been performed by others but not in detail sufficient to permit a study, for example, of the number of recrystallized grains vs. the amount of shear. In the experiments now reported, this was done with a wide variety of orientations covering nearly the entire range of slip on a single system and corresponding to amounts of shear (ratio of shearing distance to distance between lamellae) at the conclusion of a test of from 0.08 to 0.57. A particular point was made of determining the crystallite rotation, or small angular range assumed by the octahedral slip plane after these various amounts of shear. The mechanism of recrystallization and the magnitude and effect of recovery on the recrystallization process was investigated.

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† Professor of Metallurgy, Yale University, New Haven, Conn.

¹ References are at the end of the paper.

EXPERIMENTAL PROCEDURES

Preparation of Specimens

High-purity aluminum, obtained from the Aluminum Company of America, of the following composition, was used in the investigation: Si, 0.006 per cent; Cu, 0.015; Fe, 0.004; Al, 99.975 (by diff.). Single crystals in the form of rods 11 in. long by $\frac{9}{16}$ in. in diameter were made by the Bridgman method of gradual solidification of the metal from the molten condition. In selecting specimens to be used in the investigation, the solidified rods were carefully etched in Tucker's reagent,* and the

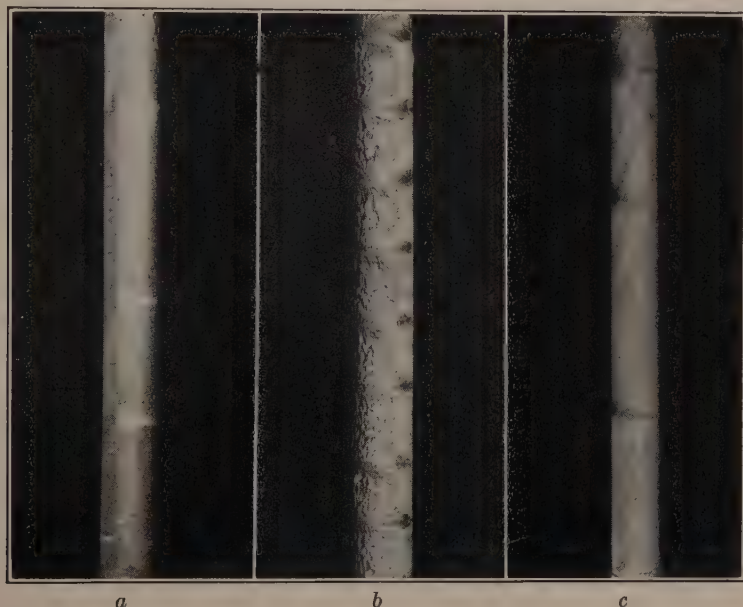


FIG. 1.—CRYSTALLIZATION BANDS IN SINGLE CRYSTALS OF ALUMINUM.

- a. Specimen in as-solidified condition, showing three bands.
- b. Specimen after annealing 24 hr. just below melting point. While in furnace right side of crystal lay on hearth. It is evident that metal between bands has softened and flowed in this direction.
- c. Strained crystal showing slip lines passing unaffected through bands.

character of the light reflections from the developed facets noted as the rods were rotated. Only those that gave perfect reflections were used.

After etching there appeared on some of the crystals a curious set of horizontal bands, Fig. 1a. An examination of the single-crystal apparatus revealed that these bands had their origin in the changing rate of crystallization induced by the temperature controller, which alternately and abruptly increased and decreased the power input to the furnace.

* Tucker's reagent is made up of 25 parts H_2O , 15 parts HF , 15 parts HNO_3 , and 45 parts HCl .

During the period in which the metal between the bands was crystallizing the furnace was slowly cooling and the point of crystallization was gradually moved further into the furnace. When the temperature dropped below that set on the controller the heating current was abruptly increased and the furnace rapidly reheated. It was during this period of rapid heating, when the actual rate of crystallization was decreased, that the bands formed.

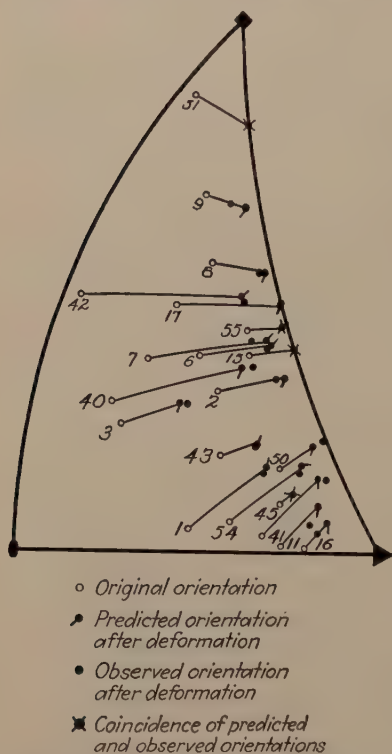


FIG. 2.—STEREOGRAPHIC PROJECTION SHOWING RELATION OF VARIOUS CRYSTALS TO AXIS OF TENSION.

In order to evaluate these bands with respect to any effect they might exert on the subsequent investigation, they were compared with the metal between the bands microscopically, spectrographically, and by X-ray analysis, and found to be identical in appearance, composition, and orientation. Their reactions to low-temperature annealing treatments were also the same. However, when held for a period of 24 hr. within 3° or 4° of the melting point, it was observed that the metal between the bands softened and flowed while the bands retained their shape (Fig. 1b). Slip lines, which formed during the subsequent straining of the crystals, were observed to pass unaffected from the bands to the intermediate metal and vice versa (Fig. 1c). It was concluded, upon the basis of these results, that the presence of these bands would have no adverse effect on the proposed

investigation, and crystals of this character were used in part of the work.

The orientations of the specimens selected by the visual examination as single crystals were determined by the back-reflection Laue method described by Greninger,² and plotted on a stereographic projection in relation to the axis of the crystal and the direction of the X-ray beam. The initial projection was rotated into two other positions: (1) with a cube pole at the center, both to facilitate the use of the Taylor and Elam projection for determining the slip system first to operate when a tensile stress is applied along the axis of the crystal, and to measure the angles between the crystal axis and the pole of the slip plane or the slip direction, respectively; (2) with the rod axis of the crystal at the center to permit

measuring the azimuth of the slip plane and the slip direction with reference to the direction of the X-ray beam.

Determination of Structure of Strained Crystals

In considering the effect of the plastic deformation on the crystallographic structure, 20 crystals, whose orientations are shown in Fig. 2,

TABLE 1.—*Elongation-shear Calculations, X-ray Analysis Results and Recrystallization Data*

Crystal	Elongation, Per Cent	Shear	ΔG per In.	Maximum Crystallite Rotations, Degrees					
				Series A ^a			Series B ^a		
				<i>P</i>	<i>N</i>	<i>L</i>	<i>P</i>	<i>N</i>	<i>L</i>
9	10.7	0.11	0.0	2.0	0.0	0.5			
45	4.0	0.08	0.0	3.0	2.0	1.0	1.0		3.0
8	13.2	0.19	0.9	3.0	1.0	0.5			
15	10.4	0.19	1.3	4.0	2.0	1.0	1.5		2.5
16	10.0	0.14	5.2	6.0	2.0	1.0			
43	8.8	0.19	0.6	2.5	0.5	0.0			
51	9.1	0.14	0.0	1.0	1.0	0.0			
55	9.0	0.19	0.0	1.5	1.5	0.5	0.0		0.5
3	10.0	0.24	0.0	7.0	2.0	0.5	3.5		0.5
11	15.3	0.23	2.3	7.0	2.0	0.5	3.5		1.0
1	25.0	0.41	13.3	11.0	2.0	1.0	7.5		0.5
2	18.0	0.32	4.5	8.0	2.0	1.0			
6	20.0	0.37	2.2	5.0	1.0	0.5			
50	10.2	0.34	1.5	4.5	2.5	1.0	2.0		1.5
7	30.0	0.48	12.0	8.0	2.0	1.0	11.0 ^b		1.0
54	22.0	0.49	4.9	10.5	2.5	0.5			
17	25.0	0.54	6.9	8.0	2.0	1.0			
40	28.2	0.57	7.8	15.0	3.0	0.5	10.0		1.5
41	24.0	0.50	5.9	6.5	2.5	0.5	5.0		1.0
42	30.0	0.56	4.6	10.0	2.5	0.5			
0	0.0	0.00		0.75	0.75	0.5			

^a *P*, positive rotation; *N*, negative rotation; *L*, lateral rotation.

^b This value is in error on the high side.

were divided into six groups of two or more each, so that the crystals in a single group possessed as widely different orientations as possible. The crystals were then deformed by tensile stressing such amounts that the shear experienced by each crystal of a group was the same but varied

from group to group. In no instance was the deformation great enough to produce complex or double slip (see Fig. 2). The elongation required to produce the desired amount of shear was calculated by the following formulas:

$$\frac{l_1}{l_0} = \frac{\sin U_0}{\sin U_1} = \frac{\sin (90 - V_0)}{\sin (90 - V_1)} \quad [1]$$

$$S = \frac{\cos U_1}{\sin (90 - V_1)} = \frac{\cos U_0}{\sin (90 - V_0)} \quad [2]$$

where:

U_0 and U_1 are the initial and final angles between the stress axis and the slip direction,

V_0 and V_1 are the initial and final angles between the stress axis and the pole of the slip plane,

l_0 and l_1 are the initial and final lengths of the crystal,

S is the amount of shear.

Following the elongation, the orientations of the crystals were redetermined and the actual values of U_1 and V_1 measured. Substituting these values in equation 2 with the original values, the observed shear was calculated (Table 1, column 3).



FIG. 3.—X-RAY PHOTOGRAPH OF $\{111\}$ SECTION CUT FROM AN UNDEFORMED CRYSTAL, SHOWING ABSENCE OF DISTORTION.

The elongated crystals were next cut in half, one-half for X-ray examinations and the other for a recrystallization study.

The crystallographic alteration resulting from the plastic deformation was studied in two series of X-ray examinations, A and B. An X-ray specimen was cut from each crystal so that the machined surface was parallel to the octahedral plane on which slip had occurred. The method described

by Pickus and Mathewson³ was used in locating the slip plane and in marking the crystals preparatory to the actual machining operations. The effects of machining were removed by carefully polishing on Nos. 1, 1 $\frac{1}{2}$, 2 $\frac{1}{2}$, and 3 $\frac{1}{2}$ emery papers and finally on a broadcloth lap, using No. 600 alundum as the polishing medium. Finally the surface was deeply etched with Tucker's reagent. A back-reflection Laue photograph taken on an undeformed crystal prepared in this manner (Fig. 3) indicated that the cutting and polishing left no detectable distortions in the specimens. The average deviation of the prepared surface from the active slip plane was 2°.

In the series A examinations the specimen was mounted in a spectrometer, so that the axis of rotation lay in the slip plane at right angles to the slip direction while the X-ray beam struck across the surface parallel to the slip direction. For the series B* examinations the axis of rotation lay in the slip plane parallel to the slip direction and the X-ray beam struck across the surface at right angles to the slip direction. In each series a sufficient number of exposures was taken at 1° intervals to determine the angular range through which diffraction from the slip plane could be detected.

Exposures of 8 min. were found to be satisfactory when only the $K\alpha$ radiation of copper was used and the X-ray tube operated at 31 kv. and 21 ma. Because of this wholly arbitrary choice of operating conditions and exposure times, the measured range of diffraction was smaller than, but directly related to, the actual range. The measured range can be taken therefore as a measure of the actual range. Such a procedure has been used in correlating and considering the X-ray results and recrystallization data.

Determination of Number of Potential Recrystallization Centers

The remaining halves of the crystals, after careful polishing and etching of the cut ends, were annealed for 15 min., at 600°C . in a furnace of high heat capacity. It was thought that the number of new grains formed by this treatment would best indicate the number of potential recrystallization centers developed by the deformation.

The amount of recrystallization was evaluated over a basic 3-in. length measured on the undeformed specimen and recorded in terms of the increase in the number of grains per linear inch by means of the following formula:

$$\Delta G/\text{in.} = \frac{(N - 1)}{(3 + 3E)} \quad [3]$$

where:

E is the percentage of elongation,

N is the number of grains counted along the length $(3 + 3E)$ in.,

$\Delta G/\text{in.}$ is the increase in the number of new grains per linear inch of specimen.

The value of N was determined by visually counting the grains which appeared on the specimen after annealing. It was frequently noticed that recrystallization occurred at several isolated places along the specimen with the result that the original grain appeared more than once. In these instances, care was exercised, by making use of light reflections from the specimen, to insure that in determining the value of N the original grain was counted only once.

* B examinations were made on only 10 of the 20 crystals studied.

Recrystallization and Recovery

An additional recrystallization study was conducted on three carefully strained single crystals, R-1, R-2 and R-3, to determine: (1) the effect of recovery on the recrystallization process, (2) the manner of recrystallization, and (3) possible orientation relationships between the new grains and the original or parent grain.

TABLE 2.—*Cumulative Annealing Schedules for Crystals R-1, R-2 and R-3*

Specimen R-1, shear, 0.20; specimen R-2, shear, 0.39; specimen R-3, shear, 0.27

Inspection Time, Min.		1.75	2.50	2.75	3.25	4.00	4.75	5.50	6.25	8.25	9.00	11.00	13.75	16.75	20.50
Temp., Deg. C.	Speci- men														
200	R-1			†				†		†		†			
200	R-2			†				†		†		†	†		
300	R-1			†				†		†		†			
300	R-2			†				†		†		†	†		
400	R-1			†				†		†		†			
400	R-2			†				†		†		†	†		
500	R-1			†				†		†		†			
500	R-2			†				†		†		†	†		
550	R-3	†	†		†	†	†	†	†		†			†	†
645	R-1			†				†		†		†			
645	R-2			*				*		*		*	*		
650	R-3	*	*		*	*	*	*	*		*			*	*

Temperatures were held constant to within $\pm 5^{\circ}\text{C}$. except for the 645°C . treatment of specimen R-2, when the limits were $\pm 10^{\circ}\text{C}$.

* Recrystallization observed.

† No recrystallization observed.

Prior to straining by elongating in a tensile machine and annealing, two flat surfaces at right angles to each other were machined along the entire length of the single-crystal rod. These surfaces were carefully polished and etched, by use of the same technique as for the X-ray specimens. The prepared crystals were elongated so that shears of 0.20, 0.27 and 0.39 (as determined by X-ray analysis) were produced in specimens R-1, R-3 and R-2, respectively. Cumulative heat-treatments were then carried out on each crystal in a constant-temperature salt bath following the schedule of time and temperature given in Table 2. At

the end of definite time intervals the crystals were removed from the bath, cooled to room temperature, etched in Tucker's reagent, and visually examined for indications of recrystallization. With the occurrence of recrystallization, the length of the new grains was measured along the common edge between the flat surfaces; that is, in a direction parallel to the axis of the crystal.

The orientations of the new grains were determined by the back-reflection Laue method. Preceding and following each heat-treatment at each temperature, a back-reflection Laue photogram was taken on specimen R-2. These photograms were taken as nearly as possible at the same location on the specimen.

EXPERIMENTAL RESULTS

Effects of Strain on Structure

The elongation of the crystals, as observed during the actual straining, was normal in all respects except one. On 11 of the 20 crystals there was a faint set of bands lying roughly in a plane whose pole was 90° from the pole of the slip plane.* Etching the crystals clearly revealed these bands and permitted the following observations to be made:

1. They extended completely through the crystals.
2. They varied in thickness and character. When viewed from one point they appeared straight and regular while from another they appeared forked and wavy.
3. When held in a certain position they reflected light strongly, as a twin would, while the remaining part of the crystal was dark.
4. Observations made on a two-circle goniometer and by X-rays indicated that the bands contained a range of orientations.

Although the data pertaining to these bands were insufficient to permit a determination of their exact relation to the deformation process, they were sufficient to arouse considerable interest and to stimulate a speculative approach to the problem. Several possible conditions were apparent that could plausibly connect these bands to the deformation process.

Plastic flow when produced in a single crystal by tensile stressing cannot take place by simple translation, owing to the constraint exerted by the grips of the tensile machine. Rather, the crystal accommodates itself to strain by flexural gliding, or *Biegegleitung*. Whether or not the bending or flexing of the glide plane occurs along the entire specimen or is restricted to a small section in the immediate vicinity of the grips is

* It is possible that the other nine crystals also contained bands of such fine structure that they could not be detected by the technique employed here; i.e., etching in Tucker's reagent.

not known. If the former condition occurs it is quite plausible that the deformation bands can be intimately associated with the bending mechanism in the layers of slip lamellae. However, if the constraint is equalized in the immediate vicinity of the grips, as is indicated by the investigation of Miller,⁴ a different relation between the bands and the deformation process must be sought.

It is not unreasonable to presume that the bands may be connected with some secondary aspect of the deformation such as the action of the plane of maximum shear stress. This particular possibility, however, was not realized in the present case because the bands were found not only at an angle approximating 45° to the axis of stress but at other angles varying through a range of at least 25° .

Another possibility is that they are the result of some form of crystal fragmentation and rotation similar to that proposed by Barrett⁵ to explain the presence of deformation bands in strained iron crystals. It is not believed that these bands originate in growth abnormalities as elaborated by Schmid and Boas⁶ but it was not a part of this investigation to solve this particular problem, which, indeed, may be of fundamental importance in the correlation of strain and recrystallization. Barrett's recent papers on the plastic deformation of iron^{5,7} and aluminum⁸ bring renewed interest in the general subject of banded structures and much more work may be anticipated dealing with the significance of bands of all kinds in worked and annealed metal.

With the beginning of plastic deformation, marked changes occurred in the character of the spots on the back-reflection Laue films. There was a noticeable decrease in intensity of the spots as indicated by the darkening of the photographic film. In addition, the spots were no longer sharp but rather diffuse, possessing tails or streaks. Increasing amounts of deformation, while causing the streaks or tails to develop markedly, had little additional noticeable effect. With all these changes the pattern of spots on the films retained the symmetry characteristics of a single crystal, indicating that although the specimens were no longer single crystals, they were aggregates of many small crystal fragments of closely similar orientations.

The results of the A series of examinations, Table 1, in addition to corroborating the observations made on the back-reflection Laue films, gave a more detailed picture of the fragmentation process. They indicated that the elongation first produced a small general increase in the range of orientations, which must be visualized as some sort of fragmentation, and that these fragments were then rotated essentially about that [112] direction lying on the active slip plane at right angles to the slip direction and in the manner described by Taylor.⁹ These rotations have been called positive, those in the reverse direction negative, and those to either side lateral.

Maximum crystallite rotation was selected as the parameter to make the correlation with shear and recrystallization data. It was thought that this quantity would best indicate not only the movement of the crystallites but also the number of crystallites concerned.

It was observed that while the negative and lateral rotations were dependent upon shear for their development, their magnitude was independent of the amount of shear, a small shear producing as much rotation as a large shear, or more.

This is clearly illustrated in Fig. 4 where the maximum negative rotations have been plotted against shear. Inasmuch as the negative and lateral rotations react similarly to shear, only this one correlation is shown. The positive rotations, on the other hand, showed a definite trend of increased rotation with increased shear. In several instances it was noted that two or more crystals, which had been subjected to the same amount of shear, did not have the same values for maximum positive crystallite rotation. Since the crystals had been sheared the same amount, and since the shear had been produced in all instances by tensile stressing, these differences may have arisen from other factors, such as: (1) the original orientation of the crystals, (2) the degree of crystal perfection of the crystal structure, (3) inclusions of foreign material and porosity, and (4) the nature of the X-radiation.

A careful survey was made of the original orientation of the crystals in relation to the maximum positive crystallite rotations, but no relation was found that could account for the observed differences. It was concluded, therefore, that the original orientation had no effect on the magnitude of the positive rotations observed after straining. No data were at hand to permit an adequate consideration of the degree of crystal perfection as a factor governing the magnitude of the crystallite rotations. The third factor, dealing with inclusions and porosity, can safely be eliminated on the ground that neither of these conditions was noticed in any of the crystals and every precaution had been taken to prevent them. Since repeat X-ray examinations checked within the limit of experimental error, the last factor, a variable nature of the X-radiation,

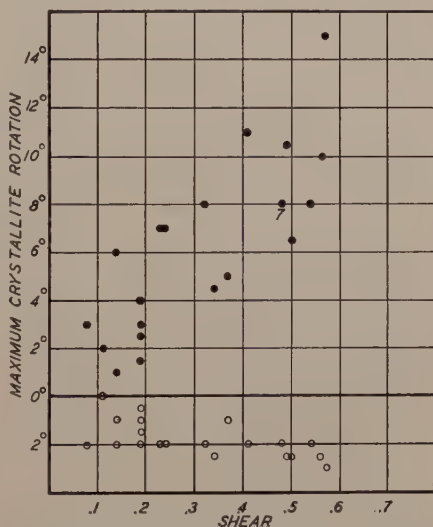


FIG. 4.—CORRELATION BETWEEN MAXIMUM POSITIVE CRYSTALLITE ROTATION (BLACK POINTS) AND MAXIMUM NEGATIVE CRYSTALLITE ROTATION (OPEN CIRCLES) WITH SHEAR.

is not operative in the present connection. This leaves the differences unexplained in any satisfactory manner, which may be taken to indicate that other factors than those considered must operate to control finally

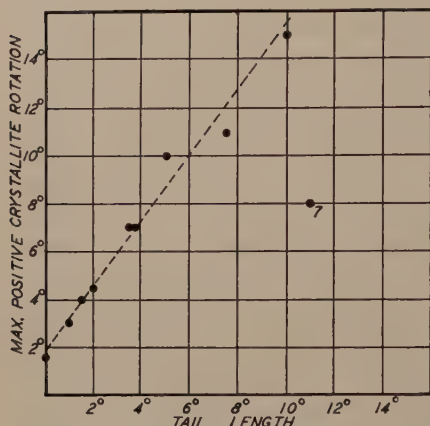


FIG. 5.—GRAPHIC REPRESENTATION OF RELATION BETWEEN MAXIMUM POSITIVE CRYSTALLITE ROTATION, AS MEASURED IN A SERIES EXAMINATIONS, AND LENGTH OF TAIL ASSOCIATED WITH DIFFRACTION SPOT PRODUCED IN B SERIES EXAMINATIONS.

the amount of maximum positive crystallite rotation that a given shear can produce. For example, Andrade and Tsien¹⁰ contend that the rotation of crystal fragments is determined not only by strain but also by stress.

Inasmuch as the B series examinations (Table 1) measured the same quantities as the A series, in a different manner, only the latter have been shown graphically. A satisfactory correlation between the two series may be seen in the straight line of Fig. 5.*

Potential Recrystallization Centers Formed by Deformation

The results of the 15-min. anneals at 600°C. (Table 1, column 4), show that increasing amounts of shear produce a corresponding increase in the number of new grains formed by recrystallization. In other words, the number of potential recrystallization centers produced by the straining is proportional to the amount of shear. This statement applies only to direct stressing; reverse stressing presents other problems.

Burgers^{11,12} has attempted to connect logically the phenomena of plastic deformation and recrystallization by proposing that recrystallization nuclei are formed in the local curvatures in the slip lamellae generated by the deformation. Germination of these nuclei, which have been characterized as strain-free crystal fragments, is determined by the intensity of the local curvature. A certain minimum intensity must be exceeded before germination can occur. Assuming that this theory is valid, it is reasonable to expect that the magnitude of the crystallite rotation resulting from the deformation should indicate fairly accurately the capacity of the strained crystal to form new grains by recrystallization. Contrary to this expectation, a rather poor correlation was found between these quantities (Fig. 6). In considering these results it must be remembered that recrystallization is intimately connected with the action

* One point corresponding to crystal No. 7 lies far away from the line, which can be attributed only to some unexplainable error in the B series datum for this crystal.

of internal stresses. The best measure of the number of the new grains that will result from recrystallization may be the intensity and distribution of these stresses. Although crystallite rotations have been freely considered in connection with internal stresses, it is, of course, possible that the maximum positive rotations observed here may not be indicative of their intensity.

Mechanism of Recrystallization

In the cumulative annealing treatments of crystals R-1, R-2 and R-3, recrystallization occurred only in the last two, and in these only after the highest temperatures had been reached. One new grain developed in the gauge length of these specimens. Observations made during the development of the new grains brought forth several interesting facts: (1) In correlation with the observations of Pickus and Mathewson,³ made on single crystals of brass, it was observed that the strained single crystals of aluminum required a markedly higher temperature to cause recrystallization than in similarly strained polycrystalline test pieces;¹³ (2) recrystallization originated in minute nuclei; (3) the linear rates of growth of the new grains into a uniformly strained crystal were constant; (4) the rate of growth of the grains varied with the crystallographic direction in which it was measured. These last two points are clearly illustrated in Fig. 7, where the length of the new grains has been correlated with the length of time the specimen remained at the annealing temperature.

The correlation for R-2 was found to be expressed by two straight lines intersecting at an abscissa value of $8\frac{3}{4}$ min. During the initial period from 0 to $8\frac{3}{4}$ min. grain No. 1, the new grain, was growing both up and down the specimen at a constant rate of 0.88 cm. per min. During this same period another new grain grew down from the grip section. At the end of $8\frac{3}{4}$ min. the two grains came together, and from that time on grain No. 1 could grow only downward. The rate of growth during the final period was 0.43 cm. per min. or one-half of the original rate. This indicated that during the first period of rapid growth, grain No. 1 was growing up and down the specimen at a constant rate, and that for the entire recrystallization period the linear rate of growth in one direction was constant at about 0.43 cm. per minute.

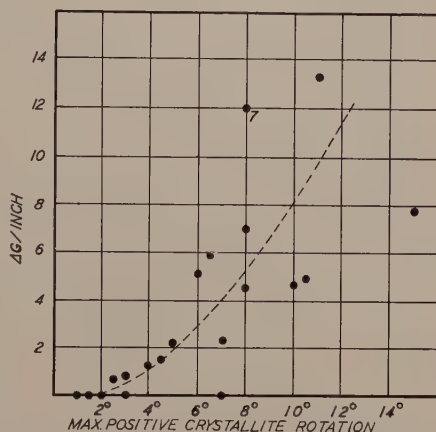


FIG. 6.—RELATION BETWEEN MAXIMUM POSITIVE CRYSTALLITE ROTATION AND CAPACITY OF STRAINED CRYSTAL TO FORM NEW GRAINS BY RECRYSTALLIZATION.

The correlation of grain length with time for R-3 corresponds to a straight line. The rate of growth was 0.60 cm. per min. This was also the linear rate of growth in one direction, inasmuch as the new grain was restricted to downward growth during the entire recrystallization by the presence of another new grain that had grown out of the upper grip section.

During the straining prior to the annealing there appeared on all three crystals the deformation bands described on page 157. These bands were found to be related to the recrystallization process as observed in crystals R-2 and R-3. The interesting point noted was that with the inception of recrystallization and for some time thereafter (up to 8 min.) the inner face between the new grain and the original crystal was a plane surface parallel to the plane of the deformation bands. It is of interest

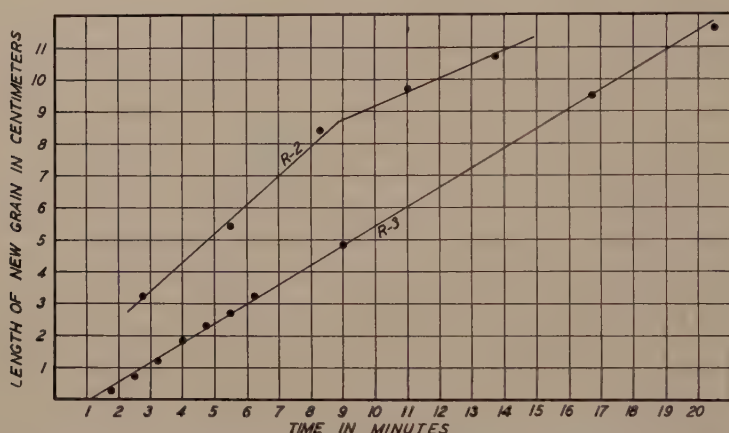


FIG. 7.—LENGTH OF NEW GRAIN FORMED DURING RECRYSTALLIZATION VERSUS TIME OF SPECIMENS AT ANNEALING TEMPERATURE.

to note that Karnop and Sachs¹⁴ have reported that the inner face of crystal growth lay parallel to the old glide plane.

The boundaries between the two recrystallized grains were not observed to move or migrate during the time of heat-treatments; that is, in neither R-2 nor R-3 did a new grain develop at the expense of a neighboring new grain.

The correlation for R-2 if extrapolated to zero time intersects the vertical axis at a finite grain size, while the R-3 correlation intersects the horizontal axis at a finite time. Neither of these intersections can be used as a basis for speculation either as to the size of the nuclei from which recrystallization starts or as to the possibility of a nucleation period prior to actual grain development, because of three factors: (1) the preceding heat-treatments, (2) length of time the specimen was at each temperature, and (3) the actual size of the specimens. The first two factors probably cooperated to cause the extrapolation for R-2 to

cross the vertical axis, and the last factor resulted in an intersection of the R-3 correlation with the horizontal axis; i.e., the grain probably existed in the specimen before it could be seen on the surface.

The orientation relationships between the old strained grain and the new grains for specimens R-2 and R-3 are shown in Fig. 8. In neither instance could the new grains be related to the orientation of the original crystal by any simple rotation. This may be interpreted as evidence against the idea that recrystallization nuclei are small strain-free crystal fragments formed by the deformation process. While this type of nucleus lends itself to the geometrical interpretation of recrystallization textures, consideration must be given to the possibility of a nucleus that forms more or less spontaneously at points of high internal stresses much

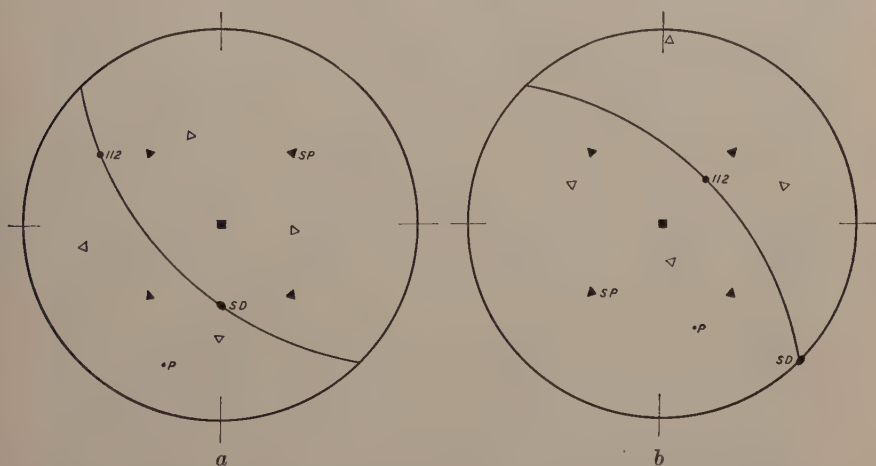


FIG. 8.—STEREOGRAPHIC PROJECTIONS SHOWING ORIENTATIONS OF THE ORIGINAL CRYSTAL (BLACK TRIANGLES), ORIENTATION OF NEW CRYSTAL (OPEN TRIANGLES), SLIP PLANE SP , SLIP DIRECTION SD , AND SPECIMEN AXIS P .
a, specimen R-2; b, specimen R-3.

as a crystallization nucleus forms in a freezing melt. From a purely speculative point of view recrystallization textures may be referred to either type of nucleus in the absence of experimental evidence permitting a definite choice.

Recovery

In view of the amount of shear experienced by the specimens R-1, R-2 and R-3, it would be expected from the preceding recrystallization data, that if recovery had no effect on the number of nuclei that could germinate, 1 to 2 grains per inch would form in R-1, 1 to 6 grains per inch in R-3, and 2 to 13 grains per inch in R-2. The fact that R-1 did not recrystallize at all and that only one new grain developed in R-2 and R-3 showed that recovery did have an effect, and that it resulted in a

noticeable decrease in the capacity of the strained grains to form new grains.

Four of the back-reflection Laue photographs taken on specimen R-2 are shown in Fig. 9. Fig. 9*a* is a photograph of the strained crystal showing the characteristic streaked-out spots which are of fairly uniform intensity except for a few high-intensity points caused by the charac-

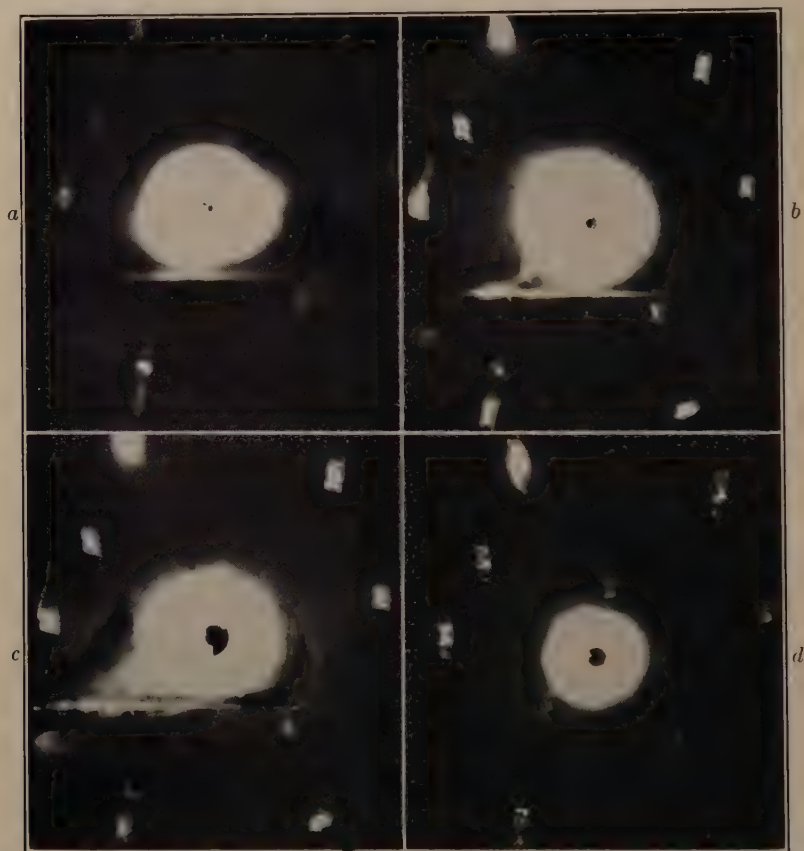


FIG. 9.—EFFECT OF RECOVERY ON STRAINED SINGLE CRYSTAL OF ALUMINUM AS REVEALED BY BACK-REFLECTION LAUE PHOTOGRAMS.

- a. Photograph of strained crystal, R-2.
- b. Same as *a* after $13\frac{3}{4}$ min. at 300°C . This photograph is also typical of structure after $13\frac{3}{4}$ min. at 200° and 400°C .
- c. Same as *b* after $13\frac{3}{4}$ min. at 500°C .
- d. Same as *c* after $13\frac{3}{4}$ min. at 645°C .

teristic radiation. Heating for $13\frac{3}{4}$ min. at 200° , 300° and 400°C ., respectively, produced new intensity maxima in the spots (Fig. 9*b*), which were still structureless and gave little indication of the changes that had occurred in the crystal. After $13\frac{3}{4}$ min. at 500°C ., however, the recovery had proceeded far enough to cause additional changes in the

spots (Fig. 9c). Here the intensity maxima were seen to be composed of many individual small spots. Tails and streaks were still present, although somewhat reduced. Fig. 9d, taken after $13\frac{3}{4}$ min. at 645°C ., shows the structure after the recovery process had presumably reached its end point. The diffraction spots were clearly observed to be made up of many small maxima, somewhat larger and more clearly resolved than those in Fig. 9c. The diffraction spots were about 4° long and 1° wide, with only the slightest indication of tails or streaks.

The development of the small intensity maxima in the diffraction spots of the back-reflection X-ray photograms have been interpreted as indicating that recovery results in a decrease of internal stress in the small crystal fragments without altering their orientations. Seljakow and Sow,¹⁵ from their X-ray study (by a rotation technique) of recovery in strained aluminum crystals, have also concluded that recovery is simply a stress-removal process.

In addition to this analysis of the X-ray results another possible interpretation should be mentioned. According to this view the small intensity maxima are the result of a coalescence of the minute crystal fragments. This concept of recovery, however, requires an explanation of the fact that coalescence does not continue until the strained crystal is again perfect, possessing the orientation of the fragment that absorbed the others. Such an occurrence has been reported only for very small deformations of 2 per cent elongation or less,¹⁶ and does not characterize the general process of softening after substantial strain-hardening.

CONCLUSIONS

1. In addition to the normal glide ellipses, the elongation generated a set of deformation bands, which lay roughly in a plane 90° from the slip plane and in the zone containing the slip-plane pole and the axis of the specimen. These bands were related in some manner to the recrystallization process.

2. The deformation first fragmented the crystals into many small crystallites with a slight increase in the range of orientations. This fragmentation was followed by a rotation of the crystallites, principally around the $[112]$ direction lying on the slip plane at right angles to the direction of the slip, and to a slight degree around the slip direction. The magnitude of these rotations was not measurably affected by the original orientation of the crystals.

3. The magnitude of the crystallite rotations was not an accurate measure of the capacity of the strained crystals to form new grains by recrystallization.

4. Recrystallization originated in small nuclei. The linear rate of growth of the new grains into a uniformly strained crystal was constant for a constant temperature. No simple relation, such as a rotation about

a single axis, was found that would rationalize the orientation of the new grain to that of the original crystal. The germinative temperature for recrystallization was markedly higher for strained single crystals than for similarly strained polycrystalline specimens.

5. Recovery occurred, to some extent, at all temperatures from 200°C. up to the recrystallization temperature, which may be as high as 645°C. Recovery resulted in a removal of internal stresses from the small crystal fragments without altering their orientation, and reduced the capacity of the strained crystals to form new crystals by recrystallization.

ACKNOWLEDGMENTS

The authors wish to express thanks to Prof. W. E. Milligan for making the spectrographic analyses, to Professors Arthur Phillips and L. W. McKeehan and to Doctors M. R. Pickus and R. M. Brick for their helpful discussions.

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DISCUSSION

(Cyril Stanley Smith presiding)

C. S. BARRETT,* Pittsburgh, Pa.—Do the data in this paper confirm Taylor's theory of rotated fragments at the slip planes, which is the basis of Burgers' recrystallization texture theory? Fig. 4 appears to, and the direction of the axis of rotation does also. However, Fig. 4 may merely represent the range of orientation from one side to the other of a deformation band—and the authors remark that such a range is common in their specimens. When a range exists with a macroscopic distribution like this the evidence for local, microscopic rotations is necessarily uncertain for it is submerged by the macroscopic effect.

As to the axis being [112] normal to the slip direction, I should like to point out that this axis is near the cross-section plane. Perhaps a number of axes lying in the cross-section plane would explain the range of orientations, as they do in the aluminum crystal deformed in compression (see page 128, this volume).

R. W. JAMES,† Cleveland, Ohio.—The author's observation that "Recovery . . . reduced the capacity of the strained crystals to form new crystals by recrystallization" is very interesting because it probably is the first time that data supporting such a contention have been recorded in the metallurgical literature, though Eastwood, James and Bell suggested that such a phenomenon might explain certain heating-rate effects (ref. 13, p. 131).

It is commonly known that slow heating of cold-worked polycrystalline commercial metals and alloys usually produces a coarser recrystallized grain structure than is produced by a more rapid heating rate, but to date no satisfactory explanation for the heating-rate effect has been offered. It seems conceivable that this effect may be the result of recovery if it is assumed that recovery treatments do reduce the recrystallization capacity of cold-worked metals. If a cold-worked material is slowly heated to the recrystallization temperature, during the heating up period the metal may "recover" to such an extent that the degree of effective cold-work is measurably reduced, hence the sample recrystallizes to a coarser grain structure. This coarser grain structure would be comparable to that produced by rapidly heating a sample that had originally received less cold reduction. With slow heating there is a relatively long period of time during which the atomic mobility gradually increases, internal stresses are relieved, various physical characteristics are altered, and there probably is some readjustment of the crystal lattice though no recrystallization, per se, has taken place. Inasmuch as all of these factors are intimately related to cold-work, it seems logical that the effective degree of cold-work has been reduced during this recovery period. An investigation along these lines has already resulted in data that tend to support this hypothesis.

J. A. COLLINS AND C. H. MATHEWSON (authors' reply).—In reply to Dr. Barrett's discussion, the authors consider that their data are best explained by Taylor's theory of crystal fragmentation and rotation,³ and therefore support this theory. However, as was pointed out (p. 160), they do not confirm Burgers' theory of recrystallization textures. Inasmuch as a range of orientations was measured in all the crystals, and deformation bands were detected on only 11 of the 20 crystals studied, it does not seem probable that this range corresponds to a macroscopic distribution inside the deformation bands as Mr. Barrett suggests. The paths traced by crystals of the large middle group shown in the projection of Fig. 2 would be closely approximated

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by slip and rotation around the corresponding [112] axis, and orientations produced at any stage of the extension remaining in the final crystal would be expected to yield diffraction spots in close agreement with those observed. The paths traced by crystals in the lower group would require, in addition to rotation around the [112] axis, some rotation of the planes around their polar axis, so that simple residual orientations found in the final crystal would not register a common [112] direction. We cannot claim that the orientation of these minute crystallites has been completely determined, but the evidence at hand is not inconsistent with the natural assumption that they are strained residual spacings along the route of extension traced by the crystal. The orientations of recrystallized grains might be attributed to some unknown form of rearrangement (nucleus formation) in these strained regions.

[The following discussion by Dr. Mehl refers also to the papers that begin on pages 41, 49, 128, 170, 193, 464, respectively.]

R. F. MEHL,* Pittsburgh, Pa.—As the result of the efforts of many workers, our knowledge of the recrystallization process has progressed rapidly in recent years. We now know that the process is one in which the variables are composition or purity, degree of deformation, temperature, initial grain size, and time.¹⁷ Excluding composition, four chief variables must be considered; if these are to be represented graphically and if final grain size is to be included as a dimension on a diagram, it would be necessary to build a five-dimensional diagram; ordinarily the so-called recrystallization diagram does not represent initial grain size or time, and for this reason must be taken as greatly oversimplified. But chiefly the disregard of the variable time has tended to mask the basically important fact that recrystallization is not an instantaneous process but one which is clearly time-dependent.

Progress in a scientific field requires the exercise of judgment in the selection of problems and modes of attack if the important questions are to be answered first. It has now been demonstrated that recrystallization proceeds by a process of nucleation of unstrained (recrystallized) grains and the growth of these grains. The time dependence of the rate of recrystallization can then be broken up into two separate processes, each time-dependent—namely, nucleation and growth—and we should be able to express the rate of recrystallization under a given set of conditions (the variables mentioned above) in terms of the rate of nucleation and the rate of growth. Mathematical methods by which known values of these separate rates may be properly associated have recently been given.¹⁸ Such an analysis must make proper allowance for variation in the rate of nucleation and in the rate of growth as the process proceeds toward completion.

It appears, therefore, that progress in the study of recrystallization will be more rapid if approached in this way; i.e., by a quantitative determination of the rate of nucleation and of the rate of growth, as these may change with the variables enumerated, including time. Some attempts have already been made (see Kornfeld²⁰ and also Karnop and Sachs²¹), though in no case do we have a full and satisfactory analysis for any given case. I think it can be said that there have been no really satisfactory determinations of the rate of nucleation; good measurements of rate of growth for a few temperatures have been made for tin (Polanyi and Schmid¹⁹), iron (Kornfeld²⁰), cadmium (Kornfeld²⁰), and aluminum (Kornfeld,²⁰ Karnop and Sachs,²¹ and

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¹⁷ R. F. Mehl: Recrystallization. Metals Handbook, 1939. Amer. Soc. Metals.

¹⁸ W. A. Johnson and R. F. Mehl: Reaction Kinetics in Processes of Nucleation and Growth. *Trans. A.I.M.E.* (1939) **135**, 416.

¹⁹ Polanyi and Schmid: *Ztsch. Physik* (1925) **32**, 684.

²⁰ Kornfeld: Series of papers in *Physikal. Ztsch.* Sowjetunion (1933–1937).

²¹ Karnop and Sachs: *Ztsch. Physik* (1930) **60**, 464.

now by Collins and Mathewson). But what we obviously need is a detailed and comprehensive study of the interplay of all of the variables with respect to the rate of nucleation and the rate of growth and an attempt to provide this for aluminum and for iron-silicon alloys is being made in the Metals Research Laboratory. With data of this sort we may hope to build an adequate theory of recrystallization and without it I believe our progress will be slow and imperfect.

It has always been difficult to find a method of expressing the degree of deformation or cold-work in terms with a physical meaning; we need this if a quantitative physical theory is to be developed. No such method exists now, though the method used by Collins and Mathewson—degree of shear in a single crystal slipping on one plane only—is at least simpler in a physical way than the rest. Their demonstration that recovery preceding recrystallization of deformed single crystals tends to decrease the number of crystals in the recrystallized piece and thus, since the rate of growth is unaffected by recovery, to decrease the rate of nucleation, is the result that would be expected and is thus more reasonable than the results of Kornfeld, who found the opposite result.²¹ Their demonstration that the rate of growth of a recrystallized grain is the greater the *smaller* the deformation shear is surprising, however, for the contrary would be expected. Kornfeld's results are satisfactory in this respect, I think. Since it is known that the rate of growth may vary within wide limits among the recrystallized grains in a single sample (for reasons not well understood), could it not be that the two grains studied represent opposite extremes in this variation, and if a large number had been measured that the average rate of growth would have been the greater the greater the degree of shear?

Recovery and Recrystallization in Long-time Annealing of 70-30 Brass

BY S. E. MADDIGAN,* JUNIOR MEMBER, AND A. I. BLANK†

(New York Meeting, February 1940)

MANY experimental and theoretical investigations have been made on the processes involved in annealing and recrystallization of metals. Most of these, however, have treated the time element as constant and heat-treatments used have been for relatively short times. Aside from the early work by Carpenter and Elam,¹ the few that have investigated the effect of time on the processes have usually done so for fairly short time periods.

During recent years the growing interest in long-time creep properties of metals and alloys under stress has made increasingly important a better knowledge of the recrystallization during prolonged heating. The recrystallization temperature of 70-30 brass given by Clark and White² in 1932 was somewhat above 400°F. (204°C.) but under 500° (260°C.), whereas in our laboratory recrystallization has been observed in creep specimens at 204°C., the lowest temperature of Clark and White's range. Since the creep properties are quite different above and below the recrystallization temperature, erroneous conclusions can readily be drawn by the application of short-time recrystallization data to creep problems.

It was thus considered of both practical and theoretical value to make long-time annealing studies near the minimum recrystallization temperature. In this way useful additions could be made to data on recrystallization temperatures and, since the reactions in this range are relatively slow, additional insight could be obtained into the factors involved in annealing.

Several comprehensive reviews of recrystallization processes have been written,³⁻⁵ therefore only a brief review of the generally accepted facts will be given here.

Though the effects of heat-treatment usually are expressed as related to observations with varying temperatures, it is logical to assume that the same order of occurrence will exist with time as a variable. Thus, we may postulate that with increasing time we will observe the following

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¹ References are at the end of the paper.

consecutive processes: (1) recovery, (2) recrystallization, (3) grain growth. The first two may to some extent be concurrent, while the last is by definition considered as occurring only after recrystallization is complete.

Recovery is generally associated with the relief of internal stress accompanied by an increase in electrical conductivity with either a slight rise or fall in mechanical properties. Mehl² states that, with temperature as a variable, the complete return of conductivity to the maximum annealed value occurs before any recrystallization is observed. No grain growth or other change in microstructure is considered as occurring here.

Recrystallization consists of the formation of nuclei and growth of the latter until the entire matrix is absorbed in new grains. This process is considered responsible for the major changes in mechanical properties, but is not generally held to be responsible for much change in electrical properties.

In an isothermal study with time as a variable, it cannot be assumed by analogy that complete recovery of electrical conductivity occurs before recrystallization sets in. It is possible that at recrystallization temperatures the two processes are active concurrently.

Grain growth is simply the increase in grain size by coalescence after recrystallization is complete, and does not have much effect upon the discussed properties—neglecting machining, cupping, etc.

Carpenter and Elam¹ in their early work and, more recently, Bungardt and Osswald⁶ have reported the growth of existing crystals without any recrystallization process. However, as stated by Masing⁷ in criticism of Bungardt and Osswald's work, little credence is given today to the existence of such a phenomenon in strained material, because experimental data show that while unstrained crystals may coalesce, strained crystals do not grow until recrystallization sets in. No consideration seems to have been given to the possibility that, after light reductions, annealing may cause softening without recrystallization of some of the worked grains and thus allow these grains to grow by coalescence without any previous nucleation.

By analogy with the laws for effect of variable temperature we may also state that:⁸

1. The time for the beginning of observable recrystallization will increase with decreasing amounts of cold-work, increasing initial grain size, and decreasing temperature.

2. The grain size of the completely recrystallized material will increase with increasing initial grain size and decreasing amounts of cold-work.

Any explanation of the phenomena observed on heating a deformed metal depends upon the concept of the state of the deformed metal itself.

To explain the changes in electrical and magnetic properties of nickel, Muller⁹ has recently postulated the existence of two orders of internal stresses in deformed metals: A stress pattern exists of microscopic but relatively long-range periodicity; superimposed on this is a short-range pattern whose period length is of the order of the conduction electron wave length. As suggested by Mott,¹⁰ the latter series of discontinuities, of the order of four or five atom distances, would decrease the conductivity by a scattering effect on the electron wave. During the process of recovery this short-period pattern is smoothed out, which causes a considerable increase in conductivity. Such superimposed patterns have been considered by others, as indicated by Desch.¹¹

How such a process would affect mechanical properties is not certain. In general, some loss in strain-hardening occurs during recovery. At first consideration this would seem to be expected from the postulated removal of short-range localized stresses. However, many investigators have reported an increase in tensile and hardness properties during relief annealing. This could be explained by assuming that the removal of the short-range pattern causes a slight increase in intensity of the longer range pattern. This could easily occur if the relation between the two was such that a peak of the short pattern fell at a minimum point in the long-range type, and a minimum of the short-range type fell at a maximum of the long-range type. Then on smoothing out the short-range pattern, the highest points would be raised to the normal position for the long-range pattern, and a similar lowering would occur at the minima. Such a process could readily cause a directional redistribution of stresses like that reported by Pickus and Mathewson¹² and others.

Several investigators have attempted to give an explanation of recrystallization phenomena in terms of nucleation and growth. Johnson and Mehl¹³ assumed that both nucleation rate and growth velocity are constant throughout the process; the process of nucleation was considered as random. Remarkable success was attained for the cases considered. Avrami, in a discussion of that paper, indicated that the nucleation rate decreases more rapidly than can be explained by the decrease in untransformed matrix. This, he suggested, is due to the existence of germ nuclei, which become activated during annealing. This could as readily be explained as follows: Accepting the usual postulate that nucleation occurs at points of high stress concentration, the nucleation rate is dependent upon the number of such points present. This is considered by Johnson and Mehl as decreasing only by nucleation; i.e., the number of nucleation points is proportional to the amount of untransformed material. However, by a process of thermal rearrangement it may be possible for the atoms to proceed in either of two directions: (1) a short-range rearrangement may take place, which results in the formation of a nucleus; (2) a longer range readjustment may occur, which results in the

removal of the stress concentrations and a softening of the original lattice. The latter process would cause a decrease of possible nucleation points and would thus cause a fall in nucleation rate faster than would be expected from the amount of untransformed matrix.

Referring again to Muller's postulate, it would seem that during recovery the short-range stress pattern is relieved by a thermal rearrangement. This results in an increase in electrical conductivity, but is not associated with recrystallization. A possible second stage in conductivity increase may be associated with removal of stress by recrystallization nucleated at the points of stress concentration in the long-range pattern. However, it may as readily be partly caused by a further stress relief action occurring now on the postulated long-range pattern.

EXPERIMENTAL PROCEDURE

Because of its generally favorable properties in regard to microscopic studies, and because the recrystallization data were desirable for a creep investigation already under way, a 70-30 brass was chosen for this investigation. To reduce the effects of impurities to a minimum, a special lot was cast from an induction furnace, all precautions to avoid contamination being observed. The analysis is:

Copper.....	69.93 to 70.23
Iron.....	0.003 to 0.004
Lead.....	0.015
Tin.....	0.001
Zinc (by diff.).....	29.75 to 30.05

A 400-lb. billet of this lot was extruded to 1-in. rod and then reduced by wire-drawing to a final diameter of $\frac{1}{8}$ in., with various tempers and grain sizes. By proper choice of drawing series and anneals, the final grain sizes and reductions shown in Table I were obtained. All specimens received an 84 per cent reduction in area between the penultimate and final anneals and care was taken to avoid any abnormal conditions in other stages of the drawing series. For the lowest final reduction of $\frac{1}{2}$ B. and S. number (11 per cent reduction in cross section), most of the working in ordinary wire drawing occurs in the outer layers. For this case a second lot was prepared by stretching to the same reduction, thus ensuring fairly uniform deformation throughout the cross section. All drawn material was straightened by a conventional method used in manufacture of wire. Specimens were then cut into 20-in. lengths for the annealing studies.

Anneals were made at 204° and 260°C. for various times from $\frac{1}{2}$ hr. to 2740 hr. Annealing was carried out in a forced convection hot-air furnace designed for creep testing and having fairly low temperature gradients. All wires to be annealed at a given time and temperature

TABLE 1.—*Record of Experiments*

Group	Estimated Grain Size, Mm.	Reduction in Area, Per Cent	Hours to Beginning of Recrystallization		
			Conductivity	Mechanical Properties	Microstructure 1000 ×

260°C. ANNEAL					
1-1	0.010	Stretched 11	Recrystallization doubtful though grain growth occurs.		
1-2	0.040	Stretched 11	No visible recrystallization.		
1-3	0.150	Stretched 11	Grain growth without visible recrystallization.		
2-1	0.010	Drawn 11	5	25	5
2-2	0.040	Drawn 11	627	125	25
2-3	0.150	Drawn 11	627	25-125	125
3-1	0.010	21	5	25	5
3-2	0.040	21	5	25	25
3-3	0.150	21	627	125	627
4-1	0.010	37	1-5	5	$\frac{1}{2}$ -1
4-2	0.040	37	5	5	25
4-3	0.130	37	5-25	25	25
5-1	0.010	60	$< \frac{1}{2}$	$\frac{1}{2}$	1
5-2	0.040	60	$< \frac{1}{2}$	$\frac{1}{2}$	1
5-3	0.130	60	$< \frac{1}{2}$	1	$\frac{1}{2}$ -1
6-1	0.010	84	$< \frac{1}{2}$	$< \frac{1}{2}$	$\frac{1}{2}$
6-2	0.040	84	$< \frac{1}{2}$	$< \frac{1}{2}$	$< \frac{1}{2}$
6-3	> 0.200	84	$< \frac{1}{2}$	$< \frac{1}{2}$	$< \frac{1}{2}$

204°C. ANNEAL					
1-1	0.010	Stretched 11	Some increase in grain size.		
1-2	0.040	Stretched 11			
1-3	0.150	Stretched 11	Grain growth without visible recrystallization.		
2-1	0.010	Drawn 11			
2-2	0.040	Drawn 11	197		2740
2-3	0.150	Drawn 11	627		
3-1	0.010	21	627		2740
3-2	0.040	21	2740		2740
3-3	0.150	21	2740		
4-1	0.010	37	125	627	627
4-2	0.040	37	627	627	2740
4-3	0.130	37			2740
5-1	0.010	60	40	15-125	15-125
5-2	0.040	60	40	15-125	125
5-3	0.130	60	125	15-125	125
6-1	0.010	84	5-15	15	5
6-2	0.040	84	15	15	15
6-3	> 0.200	84	15	1	1-15

were placed together in the furnace in a mounting that allowed adequate circulation of air between specimens. An additional wire was placed at the center of the bundle and thermocouples were attached at the extremities and center of its length. Tests showed that the heating rate and temperature gradient were approximately the same at the center and edges of the bundle, since heating was produced by convection, not radiation.

The times required to reach maximum temperature were 7 min. at 204°C. and 12 min. at 260°C. Because of the relatively slow reaction rates, it was felt that this rate of heating would not cause any appreciable error. However, for the $\frac{1}{2}$ -hr. and 1-hr. anneals, oil baths were used where the heating time was only 2 min. Fairly close checks were obtained between furnace heating and oil-bath heating for 1 hour.

The temperature distribution over the specimen length was as follows: at nominal 260°C., from 256° to 259°C.; at nominal 204°C., from 200° to 204°C. No temperature gradient was observable in the oil bath. The variation of temperature with time was $\pm 0.5^\circ\text{C}$. at both temperatures.

For each condition and time one specimen was annealed and tested and the variation in the different properties was observed. Check tests were then run for points where critical changes occurred in the various properties. In this way check specimens were not annealed at the same time and were not subjected to the same series of possible furnace fluctuations. After annealing, all specimens were given a short pickling treatment in 10 per cent H_2SO_4 .

To detect changes due to annealing, measurements were made of conductivity, tensile strength, elongation and Rockwell hardness. These results were correlated with microscopic observations.

Since conductivity values seem to be extremely sensitive to slight inhomogeneities in a metal, extreme care was taken with these measurements. As changes in conductivity rather than absolute values were important here, a system was used that was considerably more sensitive to changes than the ordinary Hoopes conductivity bridge. This apparatus was essentially an application of the voltage-drop method of resistance measurement.

Several specimens were placed in series with each other and with a standard specimen, so that the same current passed through each of them. Potential contacts were made across a 16-in. length of each specimen by means of stationary copper knife-edges. The chief error in such a method is in the determination of length. To prevent errors in length due to bending of the specimens, square-cut grooves were milled into a Bakelite slab so that the specimens would just fit with the application of a slight pressure. The knife-edges made contact with the specimens at the bottoms of these grooves. The potential drop across the 16-in. length of a specimen was measured by means of a Leeds and Northrup

potentiometer with a sensitivity of 0.001 mv. and a full-scale reading of 15 mv. Relative resistance values were obtained by comparing directly the potentiometer readings across a given specimen and across the standard specimen. Working near the full-scale potentiometer reading and replacing a given specimen always in the same position, it was possible on removing and reinserting specimens to obtain check values within ± 0.02 per cent. All values were checked in such a manner.

By inserting specimens in the same position in the apparatus both before and after annealing, the same error from the nominal length of 16 in. was made at each time and changes in relative resistance of 0.02 per cent of the initial value could be observed. Errors of about 0.1 per cent could be caused by room-temperature fluctuations. Therefore all resistance readings were made at 0°C. after the system had been allowed to reach an equilibrium value. As weight losses due to annealing and pickling were always less than 0.02 per cent, no correction was made for this factor.

During annealing, changes in density of the metal may occur. No attempt has been made to measure these changes. However, from available data it can readily be shown that this would have only a small effect upon conductivity values in the experiments described. Thus relative conductivities could be determined directly from the resistance values. Results are shown graphically as the ratio of annealed conductivity to initial conductivity.

For the microscopic studies, samples were chosen from the center and ends of each specimen. In order to facilitate the differentiation between the original grains and the new ones, all samples were polished as nearly as possible in a plane parallel to and containing the wire axis. In this way distortion in shape of the grains due to working could be used for the identification, in addition to size and the presence of deformation lines in the grains.

From each wire there were thus left two sections of about 8 in. in length, upon which tensile strength and elongation determinations were made. Where these checked closely, an average value was plotted. However, in some instances, especially just after new grains could be observed under the microscope, at which time the material was in a non-homogeneous condition, considerable differences were observed between the two sections. For these cases both observed values were plotted. Rockwell hardness and elongation values were not included in the report because neither indicated any changes that were not clearly shown by the tensile-strength data.

DISCUSSION OF RESULTS

As can readily be seen from the curves (Figs. 1 to 6), during the initial stage of heating the conductivity rises sharply to a region of fairly

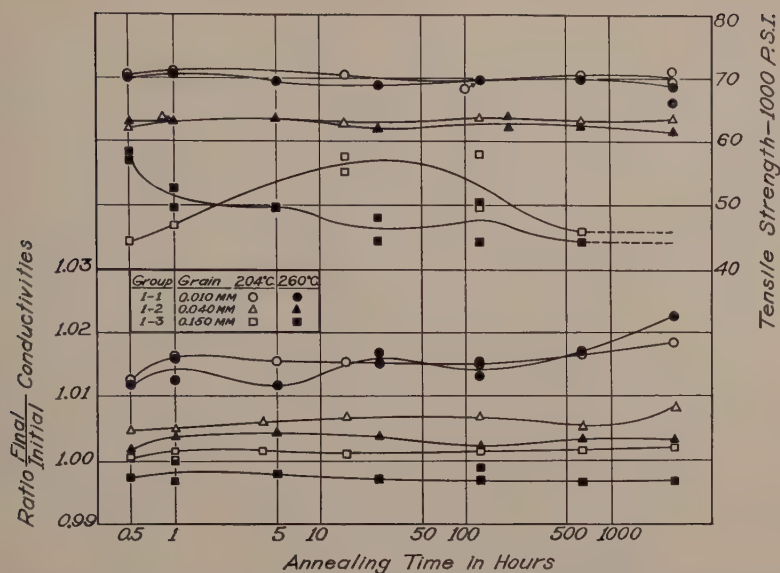


FIG. 1.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS STRETCHED TO 11 PER CENT REDUCTION IN CROSS SECTION.

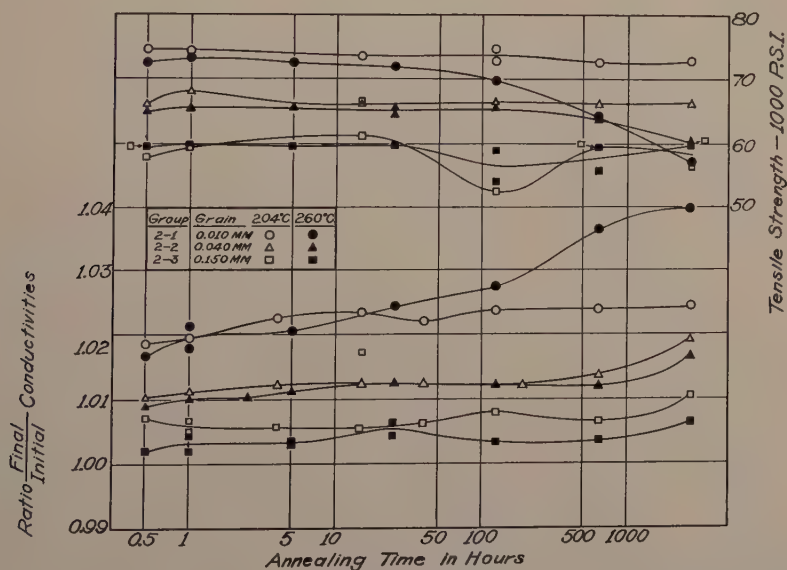


FIG. 2.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS DRAWN TO 11 PER CENT REDUCTION IN CROSS SECTION.

constant value. During this same stage, in general a slight rise in tensile properties is to be seen occurring simultaneously with the conductivity change. Under the microscope at 1000 diameters no trace of new grains can be found in this time range. Apparently this is a region of pure recovery, though possibly nucleation has already occurred at some points.

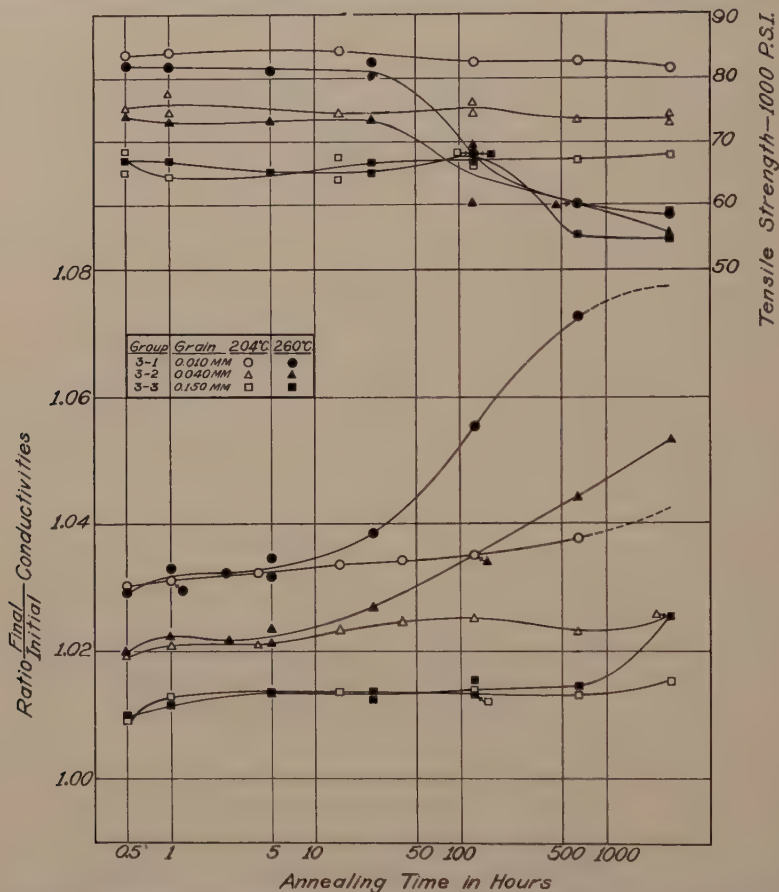


FIG. 3.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS DRAWN TO 21 PER CENT REDUCTION IN CROSS SECTION.

At the time at which new grains can first be seen, a second rapid rise in conductivity begins simultaneously with rapid changes in mechanical properties. The close relation between the first microscopic evidence of recrystallization and that given by the sudden changes in conductivity and tensile strength is clearly indicated in Table 1. The electrical and mechanical properties continue to change for a period during which increasing amounts of new grains can be observed. At the same time all indications of deformation lines in the old material gradually fade out.

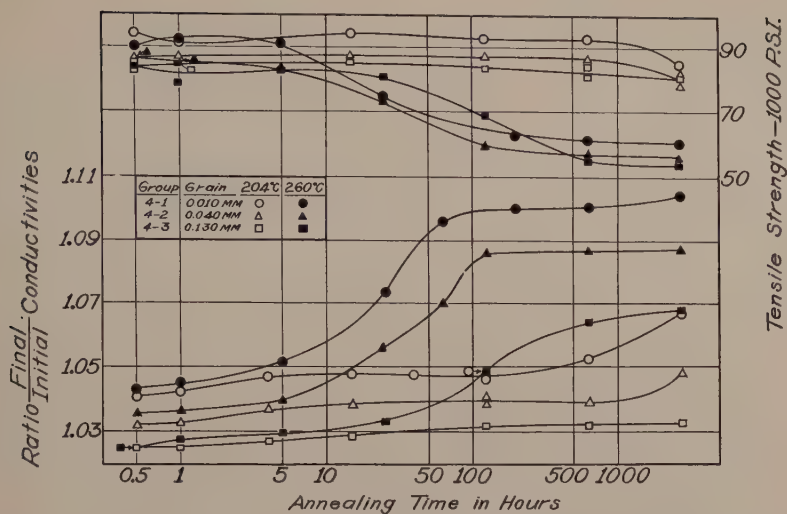


FIG. 4.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS DRAWN TO 37 PER CENT REDUCTION IN CROSS SECTION.

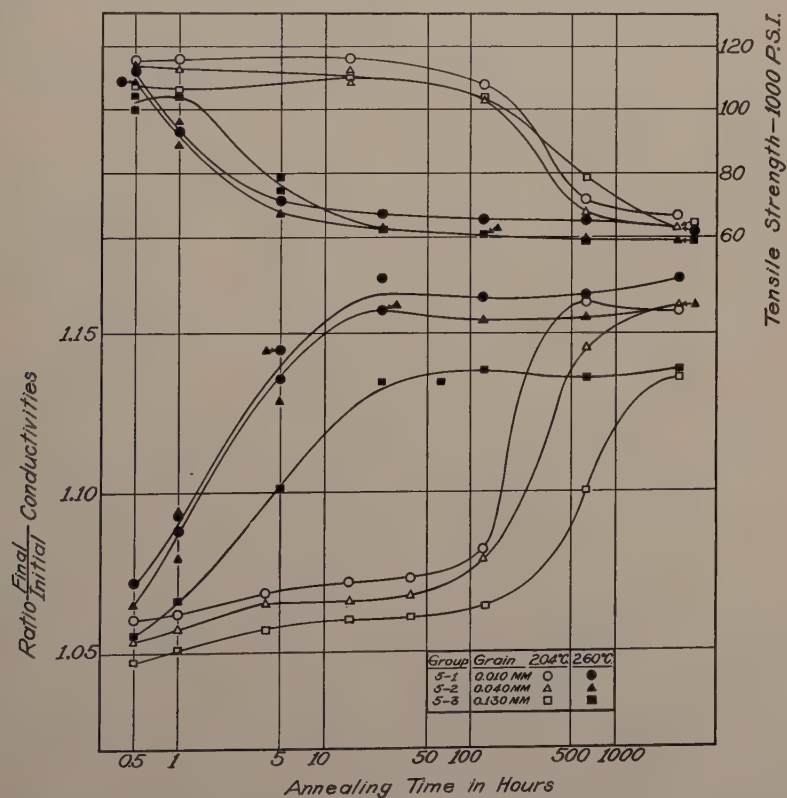


FIG. 5.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS DRAWN TO 60 PER CENT REDUCTION IN CROSS SECTION.

Finally, both conductivity and mechanical properties level off at the same time to approximately constant values. At this stage, however, recrystallization is not complete as identified by microscopic examination. Deformation lines can no longer be clearly seen and the entire specimen has the appearance of annealed material. However, by an inspection of

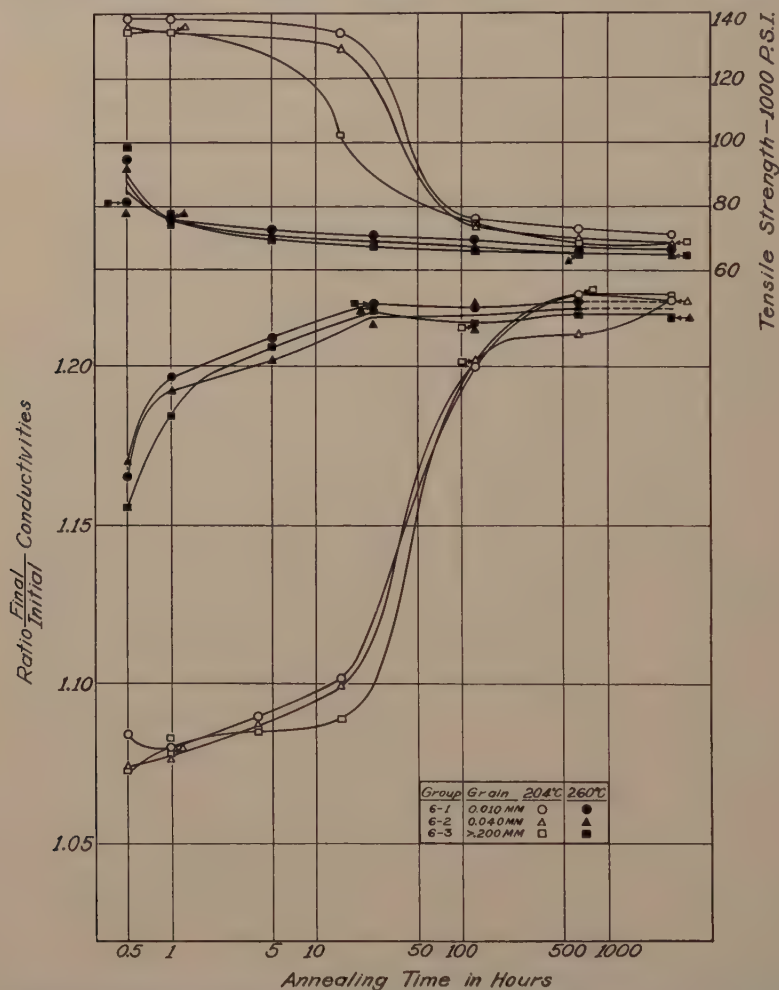


FIG. 6.—EFFECT OF ANNEALING TIME AT 204° AND 260°C. ON CONDUCTIVITY AND TENSILE STRENGTH OF 70-30 BRASS DRAWN TO 84 PER CENT REDUCTION IN CROSS SECTION.

grain sizes at successive annealing times it can readily be seen (at least in the larger initial grain sizes) that at this stage a considerable proportion of the material has a grain size relatively larger than the new grains and corresponding in size and shape more closely to the old grains than to the new. At subsequent times such grains are smaller and fewer in

number, become more irregular in outline, and have many reentrant regions in the boundary, whereas the new grains appear to have definite and regular boundaries.

It appears evident, therefore, that mechanical and electrical properties change simultaneously and probably are controlled by the same internal properties, but these changes cannot be attributed solely to the formation of new grains, and it appears that some softening occurs in the untransformed material at the same time that recrystallization is proceeding.

Electrical Conductivities

In the time range just before the first new grains are visible, the conductivity values are fairly constant, although in some cases, particularly at low degrees of reduction, a slight drop in conductivity is observed in this region. Such drops are most evident in Figs. 1 to 3; e.g., in Fig. 1 group 1-1 annealed at 260°C. for 5 hr.; in Fig. 3 group 3-2 annealed at 204°C. for 625 hr.; and group 3-2 annealed at 260°C. for 2½ hr. Careful inspection of the curves reveals several other examples.

If the hypothesis that some softening occurs in the matrix simultaneously with new grain formation and growth is accepted, the number of nuclei formed during the early stages must be much greater than that required by a constant nucleation rate in order to produce the same recrystallized grain size. Such nuclei, being softer than the matrix, are discontinuities which, if of the proper size, may have an effect on conductivity in the same direction as discontinuities caused by stress concentrations. In the early stage of their existence they should be of the same order of size¹⁴ as that postulated by Mott for electron-wave interference. Thus if present in sufficient number they would be expected to cause a drop in conductivity.

It must be remembered, however, that the recovery process may be concurrent with the nucleation and that the two stages of recovery postulated here may overlap. It would thus be only under favorable conditions that the suggested nucleation effect could be observed. Such an explanation for this anomaly can be considered only as tentative and is being investigated further.

At the higher degrees of reduction (60 and 84 per cent) a second anomaly exists, as in Figs. 5 and 6, just after the main rise in conductivity has occurred. After reaching a maximum value, a small drop in conductivity is observed followed again by a rise to the maximum value. To explain this feature it must be remembered that conductivity decreases with increasing amounts of grain-boundary material, owing to the stress discontinuities existing in the latter. Again, in the alloy under investigation, the effect of low degrees of deformation on electrical and mechanical properties is fairly small. Thus at the first maximum value we may postulate, as indicated by microscopic observation, that along with the

new grains a large amount of the matrix still exists but in a considerably softened condition. Such a postulate is supported by Trillat.¹⁵ Although the matrix material doubtless retains some slight strain, the effect of this on conductivity is small, and the alloy becomes a softened material consisting of mixed large and small grains. On further annealing, the small new grains grow and perhaps increase in number, so that the matrix material is further absorbed and at the same time, owing to increasing size of the new grains, the total grain-boundary surface is greater. Because of this increase, a decrease in conductivity can be expected. As growth continues, a stage is reached at which the total grain-boundary surface is less than it was at a somewhat earlier stage, owing to impingement and possible coalescence of the new grains as the matrix completely disappears. On this basis an increase of the conductivity could be expected. Such a process should increase in magnitude with increasing grain size, as is seen to be true in groups 5 and 6 (Figs. 5 and 6).

Nucleation Points

While it is very difficult to observe the positions of new grain formation after extreme deformation, it is evident that in general nucleation first occurs at grain boundaries and twin bands. This is true at least for lower deformations as shown in Figs. 7 and 8.

For higher deformations, however, it is possible that stresses inside the grains may be sufficiently high to cause nucleation in the interior rather than at the boundary of the grain. Such a process was observed in group 5-3 (60 per cent reduction, 0.130-mm. grain size). After only $\frac{1}{2}$ -hr. anneal at 260°C., a rather unusual structure appeared, consisting of bands running roughly perpendicular to the wire axis, even at the edge of the specimen, whereas the heaviest deformation lines existing in the as-worked sample seem to be in the general direction of the wire axis. In the as-worked sample only very faint traces of such a cross structure could be detected, the sample on the whole showing no such phenomenon (Fig. 9). After the $\frac{1}{2}$ -hr. anneal, on the other hand, the banded structure as seen in Fig. 10 existed throughout the sample, the bands having an appreciable width, whereas before annealing only a few very fine lines could be seen. At a magnification of 1000 diameters, the bands in one or two regions were seen to actually contain new grains, although no grain-boundary nucleation was observed (Fig. 11). A similar banded structure was developed in some grains along the direction of the main deformation lines. After longer annealing, the bands were much less numerous but most of those that still existed were observed to contain new grains (Fig. 12); the few bands that did not exhibit new grains were much less clear than previously, as were also the main deformation lines. A similar structure was observed in groups 5-2, 4-3 and 4-2.

Grain-boundary nucleation also occurred but did not appear until the cross-band nucleation was well developed.

The banded structure observed requires further consideration. In wire-drawing of a face-centered cubic lattice a preferred orientation is produced with a $\langle 111 \rangle$ direction parallel to the wire axis. Thus a set of (111) planes tends to assume a position perpendicular to the wire axis and to the plane of polishing in the photographed samples. In rolled material, deformation lines exist in a direction roughly perpendicular to the rolling direction and such lines might also be expected here, since the slip planes are (111) planes. As already indicated, however, these



FIG. 7.

FIG. 7.—GROUP 4-3. INITIAL GRAIN SIZE, 0.130 MM. ANNEALED 25 HOURS AT 260°C.

FIG. 8.

FIG. 8.—GROUP 3-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 37 PER CENT. ANNEALED 627 HOURS AT 260°C.

× 250. Etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Original magnification given; reduced approximately $\frac{1}{3}$ in reproduction.

Note: Wire axis is parallel to long sides of photomicrographs.

lines are not visible in great quantity in the as-worked specimen and appear to be made apparent by the annealing process.

As stated in Elam's review,⁴ hardening on inactive slip planes inclined to the active slip planes is greater than on the active system itself. Nucleation might therefore be expected on the inclined inactive planes before it occurs on the active system. The band systems observed here are inclined at a considerable angle to the direction of the main deformation lines visible in the as-worked sample. It is suggested therefore that the bands are evidence either of the hardening on inactive slip planes or of the nucleation resulting from it.

Since the bands become less numerous with continued annealing and those not developing visible grains gradually fade out, it is possible

that the bands are not actually nuclei but some pre-nucleation state of strain. As heating proceeds recovery may occur, causing the gradual

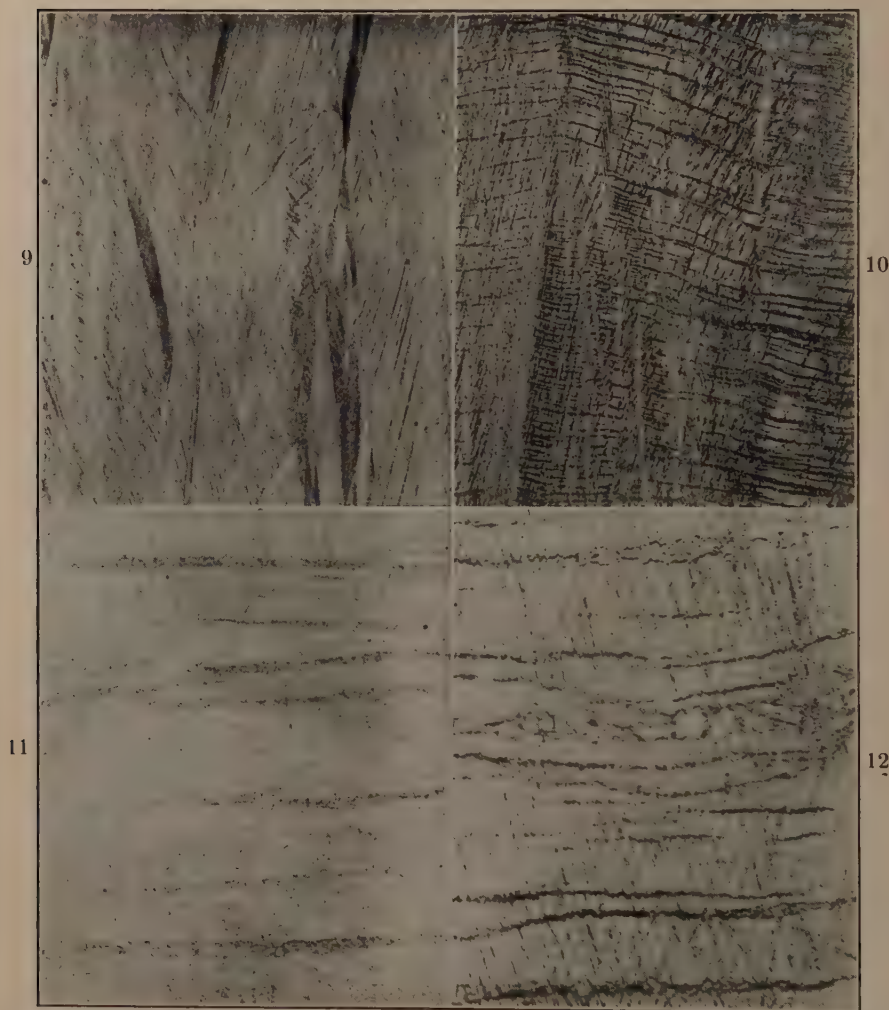


FIG. 9.—GROUP 5-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 60 PER CENT. AS DRAWN.

FIG. 10.—GROUP 5-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 60 PER CENT. ANNEALED $\frac{1}{2}$ HOUR AT 260°C.

FIG. 11.—GROUP 5-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 60 PER CENT. ANNEALED $\frac{1}{2}$ HOUR AT 260 °C.

FIG. 12.—GROUP 5-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 60 PER CENT. ANNEALED 1 HOUR AT 260°C.

Figs. 9 and 10, $\times 250$; Figs. 11 and 12, $\times 1000$. Etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Original magnification given. Reduced approximately $\frac{1}{3}$ in reproduction.

disappearance of some of the bands at the same time that the deformation lines fade out. If this does not occur, the conclusion must be drawn

that part of the nuclei are reabsorbed. This is untenable from the thermodynamic standpoint unless some straining of the nucleus occurs after



FIG. 13.—GROUP 1-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 11 PER CENT. AS STRETCHED.

FIG. 14.—GROUP 1-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 11 PER CENT (STRETCHED). ANNEALED $\frac{1}{2}$ HOUR AT 260°C.

FIG. 15.—GROUP 1-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 11 PER CENT (STRETCHED). ANNEALED 5 HOURS AT 260°C.

FIG. 16.—GROUP 1-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 11 PER CENT (STRETCHED). ANNEALED 125 HOURS AT 260°C.

All $\times 50$. Etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Original magnification given; reduced approximately $\frac{1}{3}$ in reproduction.

Figs. 13 through 17 show grain growth without recrystallization.

its formation. This might occur by a pinching action on the nucleus, as follows: The nucleus exists in a band between two heavily stressed

regions. If recovery occurs in these regions, a general lattice readjustment takes place on both sides of the nucleus. This might readily cause shearing stresses in the nucleus, which would transform it into a worked small particle. Under these conditions the tendency for large grains to absorb smaller ones could cause a disappearance of such a nucleus.

Grain Growth before Recrystallization

At low degrees of deformation, growth of the original grains seems to occur without any recrystallization. As shown in Figs. 13 to 17 for group 1-3 (0.150-mm. grain size, 11 per cent reduction), the grain size after a few hours anneal at 260°C. is much larger than the original grain size. At the same time softening seems to have occurred, as indicated by disappearance of the deformation lines. Nowhere in the annealing series from $\frac{1}{2}$ hr. to 627 hr. was any nucleation visible even at 1000 diameters. It is barely possible that nucleation may have occurred in a shorter time, but this is most unlikely as in general the time for beginning of recrystallization increases with decreasing amounts of cold-work. These large grains cannot be associated with the strain-annealing method of producing single crystals because in the latter very high temperatures are used. It must be remembered that here there is a temperature of only 260°C., whereas the original grain size of 0.150 mm. was produced by an anneal at 700°C. Because of the slow reaction rates, it is not felt that the remarks of Masing⁷ in relation to the work of Bungardt and Osswald can apply here. It is suggested that softening without recrystallization occurs in some grains, which then grow by absorption of the rest.

Similar results were observed at 204°C. At both temperatures for 2740-hr. anneal, both tensile strengths and microscopic data failed to conform with the data for other annealing times. Since certain other groups also showed discrepancies for the 2740-hr. anneal, it was felt necessary to omit these results pending further study.

A further indication that grain growth can occur before recrystallization was found in group 3-3 (0.150-mm. grain size, 21 per cent reduction). As shown in Figs. 18 and 19, a considerable increase in grain size was again observed. However, after annealing 627 hr. small new grains were visible (Fig. 19), indicating that recrystallization had begun after some growth and softening had occurred in the old grains. After annealing for 2740 hr. considerable recrystallization had taken place (Fig. 20). Fig. 8 is an example from the same series.

Further work is being carried out on this subject.

Process of Softening

From a general survey of the microstructures, it appears evident that softening does not occur by recrystallization alone, but by a combination of recrystallization and recovery. The softening of old grains can



FIG. 17.—GROUP 1-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 11 PER CENT (STRETCHED). ANNEALED 627 HOURS AT 260°C.

FIG. 18.—GROUP 3-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 21 PER CENT. ANNEALED 125 HOURS AT 260°C.

FIG. 19.—GROUP 3-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 21 PER CENT. ANNEALED 627 HOURS AT 260°C.

FIG. 20.—GROUP 3-3. INITIAL GRAIN SIZE, 0.150 MM. REDUCTION, 21 PER CENT. ANNEALED 2740 HOURS AT 260°C.

All $\times 50$. Etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Original magnification given; reduced approximately $\frac{1}{3}$ in reproduction.

Figs. 18 through 20 show nucleation after grain growth of original grains.

be followed progressively. As shown in Figs. 21-23 (group 4-3; 0.130-mm. grain size, 37 per cent reduction), softening does not always occur con-

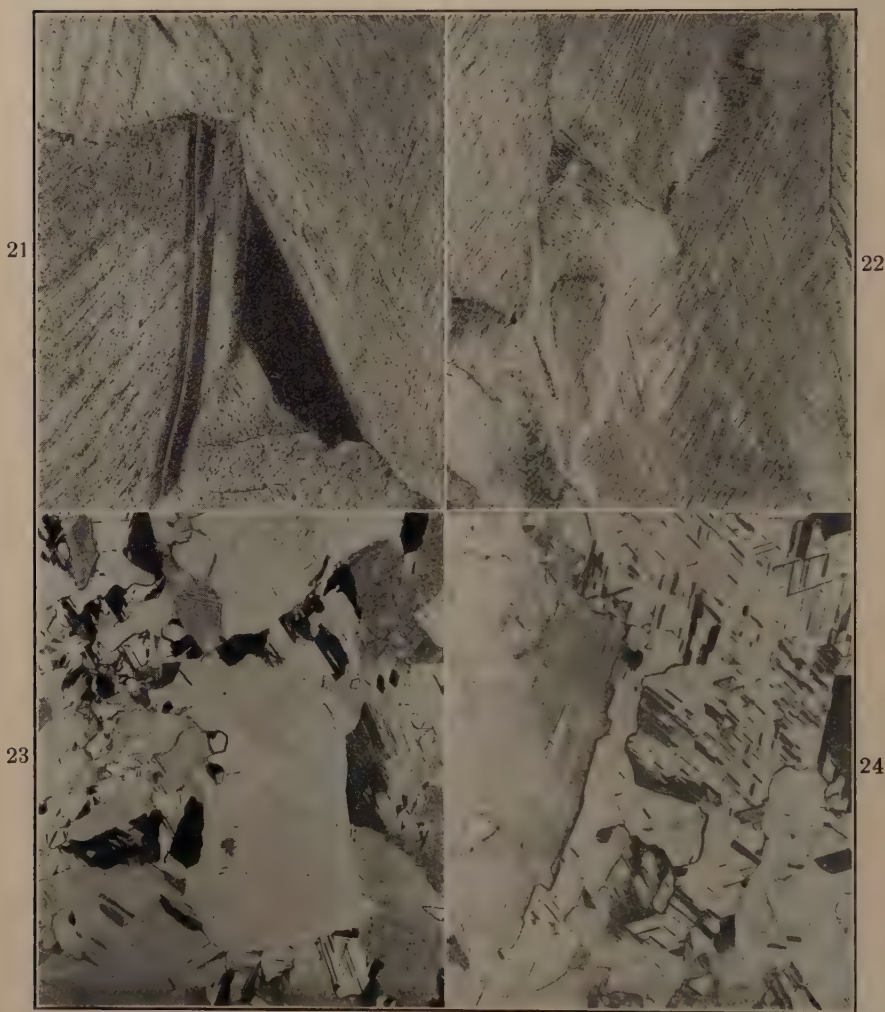


FIG. 21.—GROUP 4-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 37 PER CENT. AS DRAWN.

FIG. 22.—GROUP 4-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 37 PER CENT. ANNEALED 5 HOURS AT 260°C.

FIG. 23.—GROUP 4-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 37 PER CENT. ANNEALED 2740 HOURS AT 260°C.

FIG. 24.—GROUP 4-3. INITIAL GRAIN SIZE, 0.130 MM. REDUCTION, 37 PER CENT. ANNEALED 627 HOURS AT 260°C.

Figs. 21, 22 and 24, $\times 500$; Fig. 23, $\times 250$. Etched in $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$. Original magnification given; reduced approximately $\frac{1}{3}$ in reproduction.

Figs. 21 through 23 show gradual softening in unrecrystallized material.

tinuously throughout the specimen nor even through a single grain. Frequent examples were found where softening as indicated by disappear-

ance of deformation lines seemed to be complete in one part of a grain before taking place in other parts of the same grain (Fig. 22). In many specimens containing twin bands, one band might seem completely soft while a neighboring band would show numerous deformation lines. The latter, however, is sometimes visible in as-worked samples. The examples shown here were for a low degree of deformation. Similar effects could have been shown for larger deformations, but were less easily photographed because of the broken structure after annealing. The further progress of softening is shown in Fig. 23, in which a softened grain of the old matrix is seen in a region of recrystallized material.

It is noticeable that after softening of the matrix has proceeded to some extent a change seems to take place in the character of recrystallization. During the early stages the new grains were reasonably equiaxed and seemed to be produced by the accepted nucleation process at grain boundaries, twin bands, and the previously mentioned cross bands. After softening has proceeded for some time, however, the main process seems to be the formation of twin bands, which start as a fine needlelike structure parallel to the original deformation lines and grow through a period as seen in Fig. 24. A further study of this stage of the process is proposed.

SUMMARY AND CONCLUSIONS

An investigation has been made of the processes of recovery and recrystallization during low-temperature annealing of cold-worked 70-30 brass. Two annealing temperatures were used, one slightly above, and the other slightly below the accepted recrystallization temperature. After various annealing times up to 2740 hr., microscopic studies were made in addition to tensile-strength measurements and very sensitive conductivity measurements.

The process of softening seems to be divided into two parts: (1) a stage of pure recovery preceding any microscopic evidence of recrystallization; (2) a second stage in which recrystallization can be seen under the microscope and softening is probably a combination of recovery and recrystallization. The boundary between these stages was fixed at almost identical times by all the methods of investigation; i.e., microscopic, tensile strength, and conductivity.

Just previous to the second stage, an anomalous drop in conductivity sometimes occurs, which may be due to nucleation. A second conductivity anomaly is also observed, which may be explained by grain growth of new crystals in a softened but not completely recrystallized matrix.

For lower degrees of reduction, evidence is advanced to show that grain growth can occur before recrystallization. The temperatures used here

are well below those used for strain-annealing and also below those at which so called "abnormal" grain sizes are generally observed.

As was expected from results of previous investigators, the time for beginning of recrystallization increases with increasing grain size, decreasing amounts of cold-work, and decreasing temperature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the encouragement and counsel of Dr. D. K. Crampton, Director of Research of the Chase Brass and Copper Co. Thanks are also due to Prof. C. H. Mathewson, of Yale University, and Dr. H. L. Burghoff, for valuable criticism, and to Mr. P. A. Leichtle, who made the photomicrographs.

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DISCUSSION

(L. W. Eastwood presiding)

G. SACHS,* Cleveland, Ohio.—I wonder if the increase in electrical conductivity of the investigated brass on low-temperature anneals is related to the recently discovered fact that the alpha solid solubility in the system copper-zinc decreases with the temperature. The effect of such annealing on the conductivity is considerably larger than that observed in any other of the solid solution alloys. This apparent discrepancy is explained if a precipitation process can occur in this alloy. Have experiments been made on the effect of cold-work and of high-temperature anneals, which may give some additional information in this respect?

C. S. BARRETT,† Pittsburgh, Pa.—Some of the remarks in the paper about short-range and long-range stresses are highly speculative, but I should like to point out that a number of X-ray diffraction investigators have found the general concept of short and long-range distortions to be useful. Long-period disturbances are believed to cause a widening of diffraction lines without reducing their intensity, while short-

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period disturbances—with wave lengths of a few atom diameters—are believed to weaken the lines but leave them sharp. The conclusion of a number of investigators in the field is that the residual internal energy of cold-worked metal consists of stresses of the short-range type and not those of longer range.

The exact nature of the strain markings that are so well shown in the authors' photomicrographs continues to be uncertain. The fact that they can be made to disappear in part of a grain during recovery suggests that they may be deformation bands in which the orientation differs slightly from that of the surrounding material, and argues against their being deformation twins, whose boundaries would be expected to be more permanent. Mr. Levenson and I have observed recently striking examples of the stability of twin boundaries during recrystallization of iron. Specimens of fine-grained iron that had been elongated slightly were recrystallized to produce single crystals. The resulting crystals were found to contain many small included crystallites. An analysis of the size and orientation of these proved that they were some of the original grains that had not been absorbed by the growing crystal, and that they all had the orientation of twins of the growing grain (within a tolerance of a few degrees). In other words, boundaries that correspond to the boundaries between twins are the most stable during recrystallization.

S. E. MADDIGAN (author's reply).—From the informal discussion raised by this paper, it appears that the large changes in conductivity produced by cold-working of alpha brass have not been generally realized outside of the brass industry. This is surprising since as early as 1923 several investigators have reported such changes.¹⁶

In Table 2 our maximum conductivity changes are compared with those produced by a normal 1-hr. anneal at 1330°F. as measured with a Hoope's conductivity bridge.

TABLE 2.—*Ratio of Annealed and Drawn Conductivity*

Group	Tensile Strength as Drawn, Lb. per Sq. In.	Conductivity as Drawn, Per Cent, I.A.C.S.	Short-time Anneal at 1300°F.	Maximum Change in Long-time Anneal
2-1	72,200	27.2	1.034	1.040
2-2	65,500	27.6	1.019	1.019
2-3	59,100	28.0	1.010	1.010
3-1	79,700	26.4	1.068	1.075
3-2	71,900	27.0	1.044	1.054
3-3	66,200	27.4	1.028	1.026
4-1	89,300	25.6	1.103	1.102
4-2	84,300	26.0	1.083	1.087
4-3	83,100	26.3	1.073	1.068
5-1	107,500	24.3	1.160	1.167
5-2	106,200	24.7	1.141	1.159
5-3	102,700	24.9	1.136	1.139
6-1	126,800	23.2	1.212	1.222
6-2	121,800	23.6	1.197	1.221
6-3	124,000	23.3	1.210	1.222

¹⁶ Guillet and Ballay: *Compt. rend.* (1923) **176**, 1800.

It is readily seen that the total changes reported by us are closely checked by those of the short-time anneal; these values agree with results obtained in ordinary mill practice. Also included in the table are the tensile strengths in the as-drawn condition, which were omitted previously.

The suggestion made by Professor Sachs is worthy of careful consideration. It would seem probable, however, that any precipitation of beta phase would be greatly different for long anneals at low temperatures than for short anneals at high temperatures. However, from Table 2, the total changes are seen to be almost identical. This would seem to minimize the probability of such a reaction.

Dr. F. C. Frary has suggested an approach from the opposite side of the phase equilibrium diagram; i.e., the possible existence of an ordered structure with the atomic composition 75 per cent Cu: 25 per cent Zn. As brought out by Dr. Frary, the existence of such a structure could readily explain our conductivity results. At the time this paper was presented, a thorough investigation concerning such a structure was already under way in this laboratory. At the present time, however, the complete results are still not available.

The possible existence of such an ordered structure must be admitted, but it appears unsafe to offer an explanation based on this hypothesis without more supporting data than at present are available. The variation of conductivity with percentage reduction is almost linear, which does not agree with results obtained on ordered structures.¹⁷ Furthermore, as shown in the table, the conductivity changes are almost identical for anneals at both high temperature and low temperature. This would not be expected if an ordered structure were involved.

For carbonyl nitrogen, a double range of stress patterns was found necessary by Muller to explain the lack of congruency in the minimum temperatures at which conductivity and magnetic susceptibility changes occurred. Whether such patterns are to be discussed under the name of local distortions, as suggested by Dr. Sachs, or stress concentrations is mainly a matter of terminology, since the former require the existence of the latter. As Dr. Barrett has indicated, such a concept of double-range distortions has also been found useful by X-ray investigators. Therefore we have considered it advisable to use such an explanation for our results, at least until more definite evidence has been obtained for the existence of a superlattice.

We agree with Dr. Barrett that the strain markings may be deformation bands. Such bands and their disappearance by recovery agree with a new theory of strain-hardening developed by Prof. C. H. Mathewson.*

R. F. MEHL, discussion on page 168.

¹⁷ O. Dahl: *Ztsch. Metallkunde* (28, 133-136).

* Private communication.

Correlation of Deformation and Recrystallization Textures of Rolled 70-30 Brass

By R. M. BRICK,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February, 1940)

THE etched microstructures of cold-worked alpha brasses, after reductions in excess of about 20 per cent, exhibit dark lines or markings, which have been termed "deformation bands," "etch bands," and "strain markings." The terms will be used synonymously in this report. The markings are similar in their general appearance to etch figures found in cold-worked iron, aluminum and other cubic metals but in certain respects may differ noticeably. At reductions of from about 20 to 50 per cent in brass, they appear as straight dark lines of irregular spacing and at random directions in different grains, but apparently intimately associated with definite crystallographic planes, usually $\{111\}$, in each crystal. At higher reductions, the markings on the rolling plane tend to appear in a direction transverse to the rolling direction in all crystals but may bend away at considerable angles, particularly near grain boundaries.

Samans,¹ on the basis of X-ray and micrographic studies of two single crystals of brass, rolled to a 50 per cent reduction, showed that the lines of deformation were the edges of thin mechanical twins parallel to octahedral planes. Barrett and Levenson²⁻⁴ have made comprehensive studies of the deformation of iron and of aluminum. They show that in these two metals the deformation markings originate by division of the original homogeneous crystal into banded areas differing in orientation by an amount that increases with the degree of deformation. The markings thus cannot be twin bands, and Barrett, in a review of this subject,² attributed Samans' results on brass to an accidental choice of deformation that left the bands in approximately a twinned relationship. On the other hand, Mathewson⁵ has suggested that in some cases mechanical twinning offers a better rationalization of the coverage of some (111) pole figures of worked brass than the assumption of band rotation into symmetry positions.

Considering next a deformed and annealed alpha brass, the most striking aspect of its microstructure is the multiplicity of twin bands.

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* Instructor in Metallurgy, Hammond Laboratory, Yale University, New Haven, Conn.

¹ References are at the end of the paper.

While their nature and orientation relationships are well known, their origin remains obscure. In discussing twinning in general, Mathewson⁶ reproduced photomicrographs made by A. J. Phillips, which showed that during recrystallization of an alpha brass narrow parallel deformation bands merged to form annealing twin bands of ordinary appearance. On this evidence, he suggested that the deformation lines must be mechanical twins and the annealing twins were simply the result of growth of recrystallization nuclei in the markings. According to this view the recrystallized grains should possess the orientations of the original crystal or its four possible twins.

Confusion resulting from numerous researches and theories in this field, as cited by Barrett, have been considerably clarified by recent work of Barrett and Levenson, but it may be questioned whether their results on iron and aluminum necessarily apply to alpha brass. Without attempting to define the individual steps involved in the origin of non-effaceable strain markings and annealing twins, it appeared possible that a complete pole-figure study of cold-rolled brass and of annealed brass should tend to substantiate or to disprove the suggestions previously cited. The octahedral pole figure of cold-rolled brass might indicate whether Mathewson's suggestion in support of the twinning relation is tenable, or, to the contrary, that here the banding is of the type found by Barrett in iron and aluminum. A study of the subsequent recrystallization texture might be expected to clarify the relation between the deformed lattice and the twinned recrystallized structure. In this case, a comparison standard is available in aluminum, which generally exhibits the same type of deformation texture as brass but does not form twins on annealing, and also normally exhibits a different recrystallization texture.⁷

METHODS

The brass used in this work was a high-grade 70-30 Cu-Zn alloy with low lead, iron and other impurity content. It was available in the form of $\frac{1}{2}$ -in. mill-wrought plate, cast and homogenized polycrystalline ingot and single-crystal rod. The aluminum was available as 99.95 per cent Al metal in the form of wrought strip.

Specimens, usually about $1\frac{1}{2}$ in. square, were rolled to final thickness according to the rolling and annealing schedules of Table 1. The reductions were accomplished in several passes through laboratory power rolls; two-high polished rolls of $3\frac{7}{8}$ in. diameter. For all annealing treatments, the specimens were tightly wrapped in brass foil, to minimize surface dezincification. All anneals were for 30-min. periods in electrically heated and controlled muffles.

Where the final gauge was 0.010 in. or less, small specimens were etched in 50:50 $\text{HNO}_3:\text{H}_2\text{O}$ to a thickness of about 0.002 in. for the subsequent X-ray analysis. Thicker specimens were alternately etched as

above and ground, on both sides, on grade 0 emery paper with the final treatment an etch.

X-ray transmission photograms were taken with unfiltered Cu K radiation, using a simple box camera with a specimen to film distance of 15 mm. The specimen was mounted on a goniometer and eight exposures were taken at different angular settings of from 0 to 80°, rotating from the normal on the transverse and on the longitudinal axes. Most of the exposures were taken with a 1-mm. pinhole system, although some were made with a 1/2-mm. pinhole. The latter photograms gave sharper diffraction lines but intensity maxima could be no more accurately determined and the considerably longer exposure times led to use of the larger beam.

Readings of the positions of intensity maxima on the {111} and {002} diffraction rings were transcribed on octahedral and cubic pole-figure nets in the manner described by Barrett.⁸ Since the 0.002-in. gauge specimens were not ground to a wedge-shaped edge, the intensity and sharpness of the diffracted beam varied with the angle between the beam and the specimen. This is perhaps the source of the largest error in the construction of the pole figures, particularly with absorption of the diffracted beam at settings of about 45° from the normal. Other errors entered in the original setting of the specimen with the rolling direction and rolling plane at perhaps from 2° to 4° from the desired position. Four degrees of intensity are shown on most pole figures. These represent relative densities for that specific specimen but similarly marked areas on different figures do not necessarily have identical densities.

DEFORMATION TEXTURES

Fig. 1 shows the octahedral and cubic pole figures obtained for 70-30 brass subjected to a reduction of 99 per cent (specimen No. 1, Table 1). These are similar to those published by v. Göler and Sachs⁹ for comparable material. It is usually termed the stable end texture and may be found in many rolled face-centered cubic metals. The positions of octahedral and cubic poles in a crystal with a (110) in the rolling plane and a [112] in the rolling direction are shown as black triangles and cubes in Fig. 1. In the texture, symmetry relations are fulfilled and the mirror images of each orientation are present in approximately equal proportions.

The positions of maximum intensity of (111) poles seem to adhere well to the (110) [112] texture. Areas of secondary intensity exhibit a strong tendency of the upper and lower peripheral octahedral poles to spread toward the transverse direction, a tendency previously shown by v. Göler and Sachs. This spread indicates a considerable amount of material with a (110) in the rolling plane but with [113] to [117] in the rolling direction, a tendency confirmed by the spread of peripheral (111) poles at the transverse positions. At the center, the area of secondary intensity

forms a rough cross, which includes the kidney-shaped stronger areas. These two features of the secondary intensity areas were found in all the rolled brass specimens. The most lightly shaded areas and the open

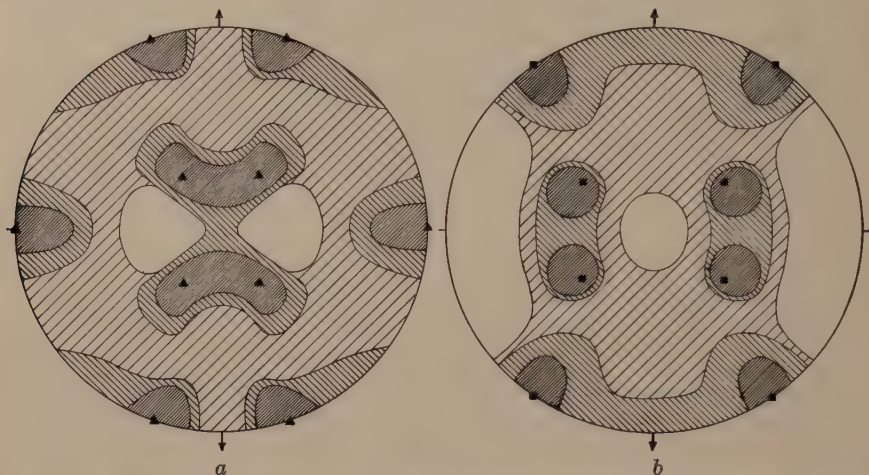


FIG. 1.—(a) OCTAHEDRAL, (b) CUBIC, POLE FIGURES OF WROUGHT BRASS ROLLED 99 PER CENT.

Triangles and cubes represent positions of (111) and (001) poles in a (110) [112] texture with complementary positions complete.

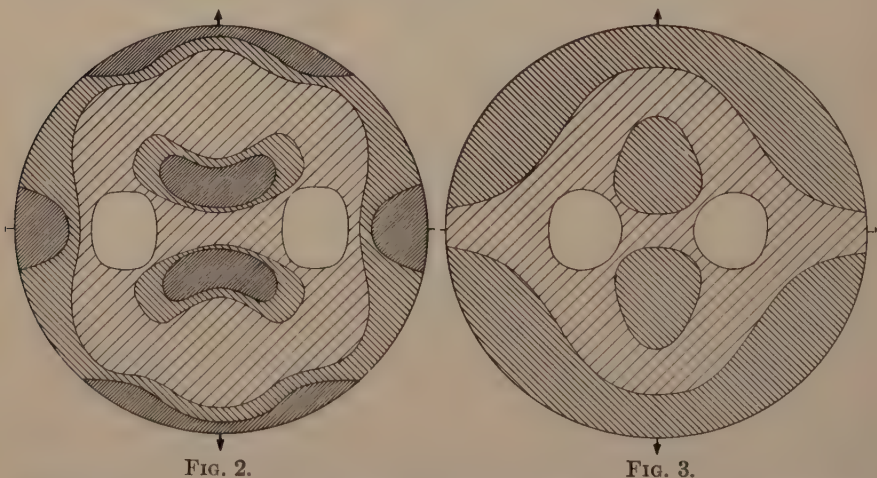


FIG. 2.

FIG. 3.

FIG. 2.—OCTAHEDRAL POLE FIGURE OF BRASS ALTERNATELY ROLLED 50 PER CENT AND ANNEALED AT 650° C. FINAL REDUCTION 50 PER CENT (SPECIMEN NO. 7).

FIG. 3.—OCTAHEDRAL POLE FIGURE OF BRASS ROLLED 96 PER CENT, ANNEALED AT 400° C. AND THEN REDUCED 60 PER CENT BY ROLLING (SPECIMEN NO. 16).

sections of the pole figure seemed to be more variable from specimen to specimen although since judgment of relative intensities by eye is more difficult in these ranges of low blackening, it might be that observational errors caused the variability. At any rate, there was always an area

nearly free from octahedral poles in the two side sections of the figure along the transverse direction.

It is certain that at this reduction of slightly over 99 per cent, not all crystals, or all parts of all crystals, are oriented in the so-called end position. A considerable amount of material lies well away from the areas of densest packing of (111) poles. The questions arise:

1. When does the (110) [112] texture become distinguishable?
2. Are the deviations from the texture attributable to entire grains, bands within grains or boundary mismatching?
3. What is the relation of strain markings and mechanical twinning to the texture?

TABLE 1.—*Specimens*

Specimen No.	Original Condition		Intermediate Steps	Final Gauge, In.	Final Reduction, Per Cent	Texture, Fig.
1	Wrought	0.500	Rolled direct	0.004	99.2 ^a	1
2	Wrought	0.500	50 per cent reduction, 650° anneal, rolled	0.004	98.5	
3	Wrought	0.500	Alternate 50 per cent reductions, 650° anneals	0.004	96.	
4	Wrought	0.500	Alternate 50 per cent reductions, 650° anneals	0.004	92.	
5	Wrought	0.500	Alternate 50 per cent reductions, 650° anneals	0.004	84.	
6	Wrought	0.500	Alternate 50 per cent reductions, 650° anneals	0.004	70.	
7	Wrought	0.500	Alternate 50 per cent reductions, 650° anneals	0.004	50.	2
8	Cast	0.240	Rolled direct	0.002	99.2	4
9	Cast	0.240	Rolled direct	0.010	96. ^a	
10	Cast	0.022	Rolled direct	0.002	90.	
11	Cast	0.022	Rolled direct	0.010	54.	
12	Wrought	0.131	95 per cent reduction, 650° anneal, rolled	0.002	70. ^a	3
13	Wrought	0.131	95 per cent reduction, 400° anneal, rolled	0.002	70. ^a	
14	Cast	0.240	75 per cent reduction, 400° anneal, rolled	0.002	96. ^a	
15	Specimen 1 above		(99 per cent reduction), 400° anneal, rolled	0.0025	75.	
16	Specimen 9 above		(96 per cent reduction), 400° anneal	0.0015	60.	
17	Single crystal 0.262		Rolled direct	0.111	57. ^a	5
18	Single crystal 0.262		Rolled direct	0.039	85. ^a	6, 22
19	Single crystal 0.262		Rolled direct	0.013	95. ^a	7, 23
20	Single crystal 0.262		Rolled direct	0.003	99. ^a	8, 24

^a Subsequently annealed at 400° for study of recrystallization texture. (All anneals for 30-min. intervals.)

Additional pole figures were constructed from X-ray photographs of other specimens summarized in Table 1. A definite texture was found at a final reduction of only 70 per cent, and even at a 50 per cent final reduction the texture varied from that found at greater deformations chiefly in the presence of (111) poles in the rolling direction (Fig. 2, specimen 7). In specimens 6 and 7, the 650° anneal before the final reduction gave a coarse-grained structure, which was not completely obliterated by the subsequent rolling procedure. The X-ray patterns were somewhat spotty and occasionally strong reflections were found slightly outside the range shown by the pole figure, indicating that some

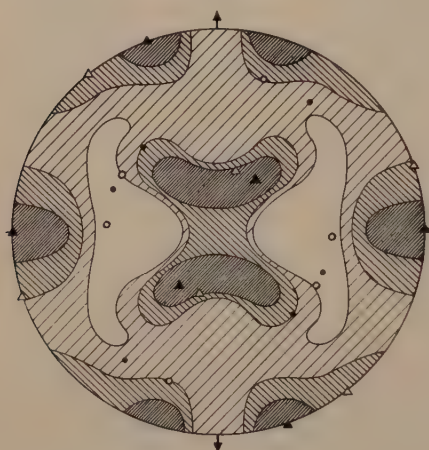


FIG. 4.

FIG. 4.—OCTAHEDRAL POLE FIGURE OF CAST BRASS ROLLED 99 PER CENT.

Solid triangles, (111) poles in a single (110) [112] texture; open triangles, (111) poles in a (110) [115] texture. Solid and open circles; hypothetical twins from central (111) poles of the corresponding textures.

FIG. 5.—OCTAHEDRAL (SOLID) AND CUBIC (DOTTED) POLE FIGURES OF SINGLE-CRYSTAL BRASS ROLLED 57 PER CENT.

Solid and hollow triangles represent original orientation of (111) poles in the single crystal.



FIG. 5.

larger individual crystals or parts of crystals had not yet rotated into the preferred position.

It was possible that the prior reductions and anneals caused the texture to be noticeable at a 50 per cent final reduction. Several experiments were performed to determine the extent of the influence of the previous history of the metal. Specimens 12 and 13 received a 95 per cent reduction, establishing a moderately strong texture. No. 12 received a 650° anneal, which resulted in a coarse-grained, apparently randomly oriented structure. No. 13 received a 400° anneal and exhibited a very fine-grained structure with a pronounced recrystallization texture. Upon subsequent rolling to a reduction of 70 per cent, the coarse-grained brass, No. 12, showed a fairly well developed (110) [112] texture whereas the

fine-grained specimen, No. 13, exhibited a nearly random orientation of crystallites. A specimen similar to the latter, No. 14, did show a moderately strong deformation texture but at a reduction of 96 per cent. Specimens 15 and 16 agreed with No. 13 in showing only faint traces of a texture after reductions of 75 and 60 per cent, respectively, of fine-grained recrystallized specimens.

The faint (111) texture of specimen 16 is reproduced in Fig. 3. There is a tendency for (111) poles to assemble in a broad band distributed around the rolling direction; also in areas in the rolling direction tilted

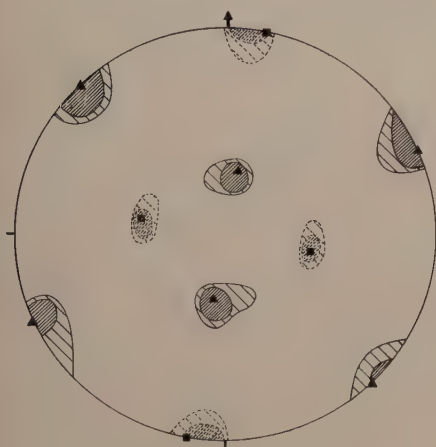


FIG. 6.

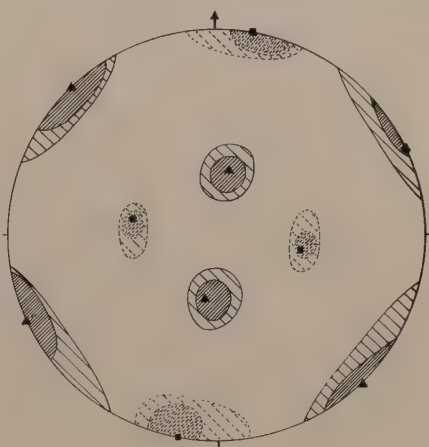


FIG. 7.

FIG. 6.—OCTAHEDRAL (SOLID) AND CUBIC (DOTTED) POLE FIGURES OF SINGLE-CRYSTAL BRASS ROLLED 85 PER CENT.

Triangles and cubes represent positions of (111) and (001) poles in a single (110) [117] orientation.

FIG. 7.—OCTAHEDRAL (SOLID) AND CUBIC (DOTTED) POLE FIGURES OF SINGLE-CRYSTAL BRASS ROLLED 95 PER CENT.

Triangles and cubes represent positions of (111) and (001) poles in a single (110) [117] orientation.

from the rolling plane. The differences in intensity of reflections in going from one region to the other in Fig. 3 are not as marked as in other pole figures and merely represent the first slightly discernible change from a random to an oriented structure.

To eliminate the influence of prior deformation, specimens of different initial thicknesses were cut from a cast and homogenized ingot. The surfaces were etched and smoothed on No. 1 emery paper to remove the zone of metal affected by the cutting operation and subsequently rolled according to the schedule of Table 1. Fig. 4 shows that after a reduction of 99 per cent, cast specimen No. 8 attained a texture comparable to the initial wrought brass (Fig. 1). In this case the metal was rolled directly to the thickness employed for the X-ray examination and was not etched while the material of Fig. 1 had been etched from 0.004 to 0.002 in.

Apparently, under the rolling conditions and metal thicknesses employed in this work, no surface texture was obtained that differed materially from that of the interior.

The position of one set of (111) poles in a (110) [112] orientation are shown in Fig. 4 as solid triangles. The positions of mechanical twins on the potentially active planes 35° from the center of the projection are shown as solid circles. The configuration of the pole figure with reference to possible twin positions shows that material in positions of mechanical twins from the (110) [112] texture is not present in appreciable quantities, nor is there better evidence of material in twin positions from the (110) [113] — [117] textures.

Specimen 9 from the cast material at a 96 per cent reduction exhibited a similar texture, although not quite so well defined. Specimen 10 received almost as high a deformation, 90 per cent, but showed only traces of a texture while No. 11 exhibited nearly single crystal reflections, many of which indicated a (110) plane in the rolling plane but a variety of crystal directions in the rolling direction. A widely different type of reflection pattern was obtained by changing the point of impingement of the X-ray beam on the specimen. Both No. 10 and No. 11, of only 0.022-in. initial thickness, were cut from cast material with grains mostly over $\frac{1}{16}$ in. in diameter. Thus the specimens had chiefly one grain, at most two grains, extending through the section.

The fragmentary nature of the above tests led to experimentation on a single crystal. A cylindrical slab, $1\frac{1}{2}$ in. in diameter and 0.262 in. thick, was chosen for rolling and analysis by the methods previously employed. The initial crystal orientation relative to the rolling plane and direction is shown in Fig. 5 by the solid (111) poles for one hemisphere, open (111) poles for the other, together with the pole figure found after a reduction of 57 per cent (specimen No. 17). The specimen was rotated 180° around the rolling direction for each pass to ensure straight flow of the metal. No record was made of which side corresponded to the initial orientation determination, although subsequently the same hemisphere is projected for the pole figure at each stage in the reduction.

In deriving the single-crystal pole figures, it was necessary to double the number of exposures by rotating the specimen in both directions from the longitudinal and transverse normals, since it was not possible to assume symmetry in the pole figure. Although the data then covered the entire spherical projection, only one hemisphere is plotted in normal density. When an area of high intensity occurs near the periphery but on the other hemisphere, it is here shown by thin lines. It was possible simultaneously to project (100) poles on the same figure and cube-plane distribution is indicated by the dotted areas.

The figure suggests that the initial orientation, with a (110) pole about 14° from the rolling plane and a [100] some 4° from the rolling direction,

has rotated during the 57 per cent reduction to place the (110) about 5° from the rolling plane with no appreciable change in direction.

A further deformation from the 0.111-in. specimen above to 0.039 in., a total reduction of 85 per cent, produced very little change in the pole figure, except for completion of the rotation of (110) into the rolling plane (Fig. 6), for specimen 18. The metal still appears to be nearly a single crystal in a (110) [117] orientation with no X-ray evidence of a complementary orientation. Upon further rolling to 0.013 in. a total reduction of 95 per cent for specimen 19, a slight trace of a complementary orientation appeared in the X-ray photographs. Fig. 7 indicates that the orientation of the crystal changed very little; the (110) pole has remained in the

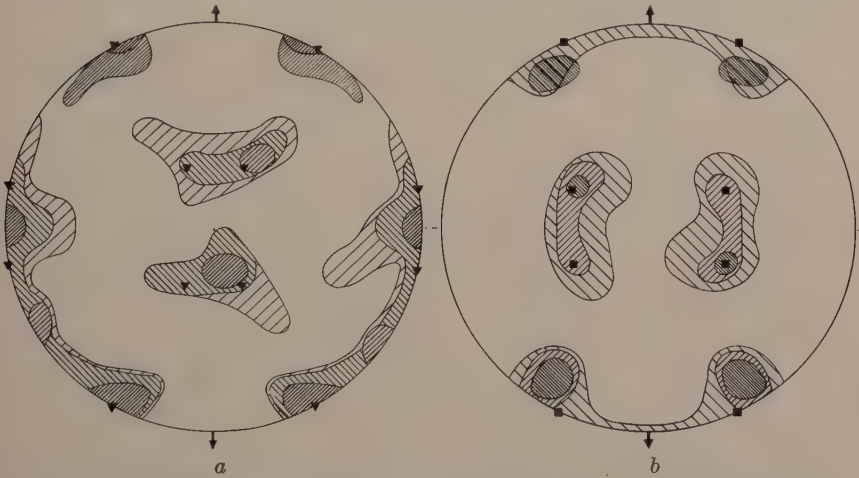
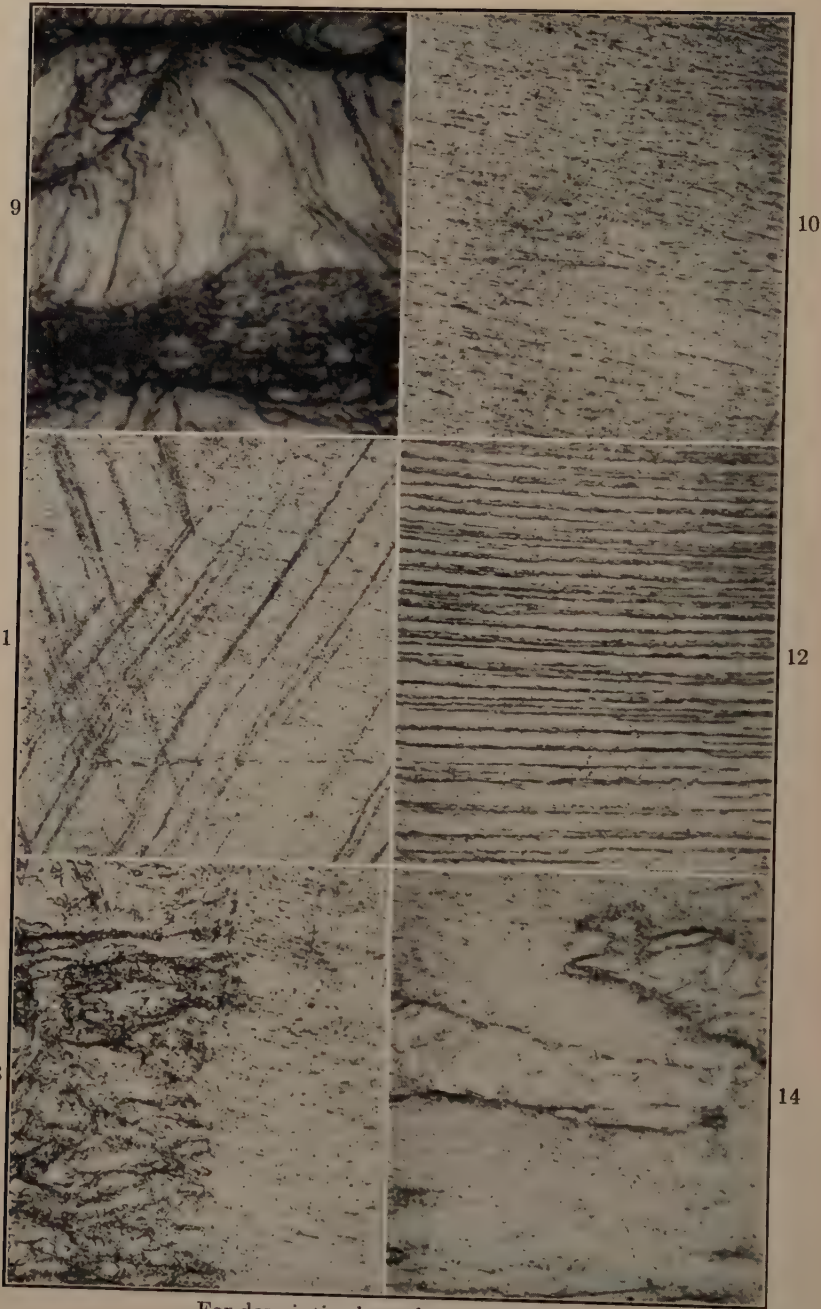


FIG. 8.—OCTAHEDRAL (a) AND CUBIC (b) POLE FIGURES OF SINGLE-CRYSTAL BRASS ROLLED 99 PER CENT.

Triangles and cubes represent positions of (111) and $\bar{1}\bar{1}\bar{1}$ poles in a (110) [113] texture with complementary positions present.

rolling plane and the (100) pole has started to rotate further away from the proximity of the rolling direction, to change from a (110) [117] toward a (110) [112]. In this condition, the onset of complementary positions may be responsible for part of the lengthening of distribution of (111) poles along the periphery, or it may chiefly be a result of bending associated with rotation of (100) from the rolling direction.

The final reduction employed was at 99 per cent, specimen No. 20. The separate (111) and (100) pole figures in Fig. 8 show that rolling from 0.013 in. to 0.003 in. for a final stage in the reduction of 77 per cent has partially changed the material from essentially a single (110) [117] orientation toward a symmetrical (110) [112] texture. The (110) has rotated out of the rolling plane toward the rolling direction by about 5° to 10° , the actual major direction is nearest [113], strong traces of the original (111) pole positions remain and while complementary orientations



For descriptive legends see page 203.

are practically complete on the periphery, the center of the figure is asymmetric.

At the several stages of reduction, the single-crystal specimens were occasionally X-rayed in several places at a critical angle of reflection. In all cases, the patterns were identical in appearance but, in accordance with Barrett's results on iron and aluminum, sometimes exhibited rotations that usually were less than 5° of arc. The area covered by the beam, a circle over 1 mm. in diameter, resulted in the integration of all crystallite orientations in that area.

Microstructures of the rolling plane of all specimens were examined and those of the polycrystalline material were found to be similar, in regard to the appearance of the etch or deformation markings, to photomicrographs of worked brass previously published. The straight, randomly oriented striae found at low reductions gradually assumed a general alignment transverse to the rolling direction but often forked and displayed elongated cellular shapes with interior "plateau" markings visible at a high magnification (Fig. 9).

The single-crystal specimens afforded a better opportunity for establishing a possible correlation of strain markings with orientation changes. After a 57 per cent reduction with a slight crystal rotation of (110) toward the rolling plane, the specimen showed none of the characteristic strong, dark etch markings but rather, in general, a fine regular pattern, which at low magnifications appeared similar to scratches made by 0000 emery paper, and at high magnifications seemed to consist of disconnected spots aligned in a nearly transverse direction (Fig. 10). In a few places, markings appeared at specific angles in generally straight lines (Fig. 11). These were at angles that were readily measured, and when checked with the corresponding pole figure, Fig. 5, appeared to be parallel to octahedral planes. One of these planes responded to shock deformation as shown in Fig. 12, representing the structure near the indentation made by an offset tooth in the hacksaw used to cut out the specimen.

At the 85 per cent reduction, with only a very slight additional change in the pole figure, the structure was practically unchanged, although in a

FIG. 9.—POLYCRYSTALLINE BRASS ROLLED 90 PER CENT. $\times 2000$.

FIG. 10.—SINGLE-CRYSTAL BRASS ROLLED 57 PER CENT. $\times 800$.

FIG. 11.—SINGLE-CRYSTAL BRASS ROLLED 57 PER CENT. MARKINGS PARALLEL TO (111) PLANES. $\times 800$.

FIG. 12.—SINGLE-CRYSTAL BRASS ROLLED 57 PER CENT. NEAR SAW CUT EDGE. $\times 800$.

FIG. 13.—SINGLE-CRYSTAL BRASS ROLLED 85 PER CENT. ONSET OF STRONGER MARKINGS. $\times 800$.

FIG. 14.—SINGLE-CRYSTAL BRASS ROLLED 95 PER CENT. NUMEROUS STRONG MARKINGS. $\times 800$.

All photomicrographs taken on rolling plane with rolling direction vertical, to correspond with pole figures. All specimens etched with ammonia peroxide.



For descriptive legends see page 205.

few well separated areas, stronger markings, generally outlining cellular spots, began to appear (Fig. 13).

After a reduction of 95 per cent, the strong, frequently cellular markings were found to occur in wide bands parallel to the rolling direction, although a greater amount of the material exhibited only the light original transverse striae. The intermediate zone showed some markings nearly parallel to the rolling direction (Fig. 14).

A specimen at a reduction of 98 per cent, although not analyzed with X-rays, would probably have shown a condition between the (110) [117] orientation and the (110) [112] texture. The microstructure exhibited a structure similar to that at 95 per cent except that there was considerably less material in bands showing light markings and more in the heavily marked bands. Under crossed, polarized light, the etched microstructure showed etch pits, which during a complete rotation exhibited four points of alternate lighting and extinction, 90° apart. At the junction of light and heavily marked bands, a sawtooth structure exhibited two periods of alternate lighting and extinction, roughly 180° apart (Fig. 15).

At a 99 per cent reduction, the entire structure showed predominantly the strong dark markings with all cellular outlines practically obliterated (Fig. 16).

RECRYSTALLIZATION TEXTURES

Specimens of sheet No. 1 (Table 1) were annealed for 30-min. periods at 50° temperature intervals from 250° to 750° C. The X-ray photographs showed that recrystallization was complete at 300° C. but that at 300° and 350° the intensity maxima of the new texture were less sharply defined than after a 400° anneal. The observation would suggest that the early stages in growth consisted in the absorption of randomly oriented grains by those situated favorably with respect to the recrystallization texture. Higher temperatures of anneal resulted in further grain growth, with the gradual obliteration of the texture, although some traces of it were visible even after a 750° treatment. The apparent loss of the texture may be chiefly related to the decrease in the number of crystals encountered by the beam in a coarse-grained specimen. It is possible

FIG. 15.—SINGLE-CRYSTAL BRASS ROLLED 98 PER CENT. POLARIZED LIGHT WITH PARTLY CROSSED NICOLS. $\times 100$.

FIG. 16.—SINGLE-CRYSTAL BRASS ROLLED 99 PER CENT. $\times 800$.

FIG. 17.—SINGLE-CRYSTAL BRASS ROLLED 57 PER CENT. ANNEALED AT 400° C. NEW CRYSTALS IN STRAIN MARKINGS NEAR FORMER SAWCUT EDGE. $\times 800$.

FIG. 18.—SINGLE-CRYSTAL BRASS ROLLED 85 PER CENT, ANNEALED AT 340° C. $\times 800$.

FIG. 19.—SINGLE-CRYSTAL BRASS ROLLED 85 PER CENT, ANNEALED AT 340° C. $\times 800$.

FIG. 20.—SINGLE-CRYSTAL BRASS ROLLED 95 PER CENT, ANNEALED AT 315° C. $\times 800$.

All photomicrographs taken on rolling plane with rolling direction vertical to correspond with pole figures. All specimens etched with ammonia peroxide.

that a mechanism for moving the sheet in front of the beam without changing its angular relationships would yield evidence of a distinct texture. In this work, however, all recrystallization pole figures were obtained on material annealed at 400°C .

The annealing texture shown by specimen No. 1 is reproduced in the octahedral and cubic pole figures (Fig. 21). It is quite similar to that described by Bass and Glocker.¹⁰ Schmid and Boas⁷ refer to it as a (113) [112] texture, although poles placed according to this orientation, as in the accompanying pole figures, are several degrees away from the center of areas of densest packing.

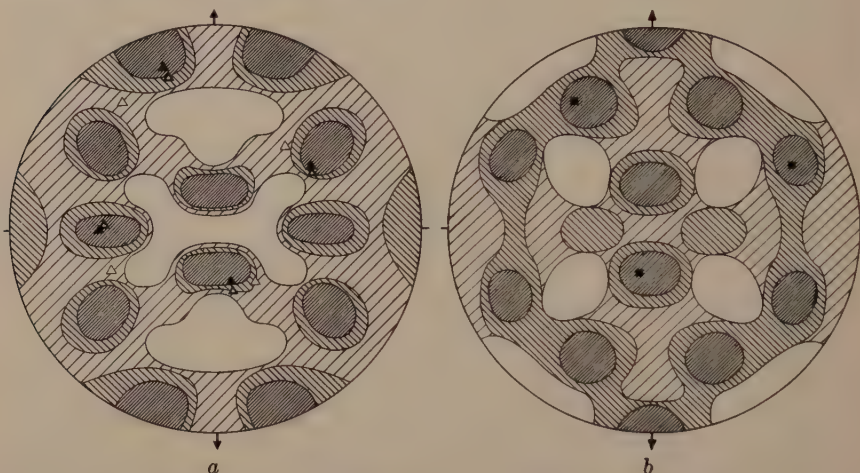


FIG. 21.—RECRYSTALLIZATION TEXTURE OF POLYCRYSTALLINE BRASS ROLLED TO A 99 PER CENT REDUCTION FOLLOWED BY A 400°C ANNEAL.

a. The octahedral pole figure. Solid triangles show (111) poles in a single (113) [112] orientation; heavily outlined triangles, positions of (111) poles of hypothetical twins from a central (111) pole in a (110) [115] orientation; lightly outlined triangles, positions of (111) poles of hypothetical twins from a central (111) pole in a (110) [112] orientation. *b.* The cubic pole figure. Cubes placed according to a single (113) [112] orientation.

The recrystallization texture shown is the only one obtained on polycrystalline specimens in this work. The degree to which the texture develops seems to be related to the strength of the deformation texture from which it is derived, although certain exceptions to the rule were noted. Specimen No. 9, which had a less well developed deformation texture than No. 1, also showed a less well developed annealing texture. Specimen No. 13, which after a 95 per cent reduction and 400°C anneal had a well developed (113) [112] texture and developed only a trace of the deformation texture upon a further 70 per cent reduction, subsequently exhibited a practically random distribution of new grains when given a second 400°C recrystallization treatment. The exception was specimen No. 12, which showed distinct evidences of a deformation texture after the comparable 70 per cent reduction of a coarse-grained aggregate but then

developed a random recrystallized structure when subsequently annealed at 400° C.

From the photomicrographs made by A. J. Phillips⁶ and the results above, it seems probable that the recrystallization texture is related to both the individual deformation markings and the general (110) [112] texture. In Fig. 21a, an attempt is made to show the possible correlation. The agreement of the (113) [112] texture with twins from the central four (111) poles of a (110) [112] deformation structure is unsatisfactory. However, if twins from material at the secondary intensity positions of the deformation texture showing (110) [113] — [117] are considered, nearly as satisfactory an agreement with the actual annealing texture is found as is yielded by the empirically chosen (113) [112] poles. The moderate intensity areas on the periphery at the transverse axis of the recrystallization texture may be considered as derived directly from the deformation structure with practically no change in orientation.

For further confirmation of this possible correlation between deformation and recrystallization textures, the rolled single-crystal specimens studied in the first section were annealed for cumulative 30-min. periods according to the schedule in Table 2.

TABLE 2.—*Annealing of Rolled Single-crystal Specimens*

57 Per Cent	85 Per Cent	95 Per Cent	99 Per Cent
340° C.	320° C.	295° C.	280° C.
350	330 ^a	305 ^a	285 ^a
360	340 ^b	310	290
370 ^a	350 ^c	315 ^b	295 ^b
380		320	300
390		325 ^c	305 ^c
400 ^b			
410			
420			
430 ^c			

^a Recrystallization started.

^b Photomicrographs 17 through 20.

^c Recrystallization completed.

The table shows the familiar effect of an increasing deformation lowering the temperature at which recrystallization is initiated and shortening the temperature interval required for its completion. The criterion for setting the temperatures at which recrystallization started and was completed was the X-ray photograms.

After a 57 per cent reduction, the rolled specimen that showed only general, light strain markings recrystallized to a rather coarse-grained structure with practically a random distribution of orientations. The recrystallization temperature was fairly high for this rather considerable

reduction. The structure at an intermediate stage of recrystallization generally showed a few relatively large new crystals in the strain-marked deformation structure. The new crystals had no obvious relationship either to the light strain markings or to the straight lines that appeared to be parallel to octahedral poles (Fig. 17; cf. Fig. 12).

The specimen reduced 85 per cent by rolling which, it will be recalled, resulted in only a few heavy deformation markings in the microstructure, recrystallized to a coarse-grained structure exhibiting a distinct non-

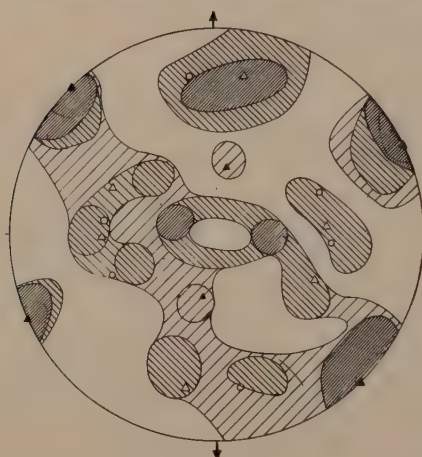


FIG. 22.

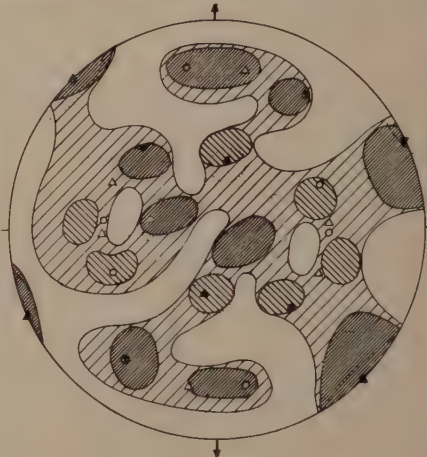


FIG. 23.

FIG. 22.—OCTAHEDRAL POLE FIGURE OF SINGLE-CRYSTAL BRASS ROLLED 85 PER CENT, ANNEALED AT 400° C.

Solid triangles, (111) poles in original (110) [117] position. Hollow triangles, (111) poles twinned from original central (111) poles. Hollow circles, twins from complementary central poles. Dotted triangles and circles, twins from peripheral original poles and their complements, respectively. Dotted areas, strong areas of deformation pole figure.

FIG. 23.—OCTAHEDRAL POLE FIGURE OF SINGLE-CRYSTAL BRASS ROLLED 95 PER CENT, ANNEALED AT 400° C.

Solid triangles, (111) poles of original (110) [117] deformation texture. Hollow triangles, twins on original central (111) poles. Hollow circles, twins on complementary central poles. Dotted triangles, twins on original peripheral poles. Dotted circles, twins on complementary peripheral poles. Crossed circles, twins on central poles of a (110) [112] orientation.

symmetrical texture (Fig. 22). Superimposed on the recrystallization pole figures are outlines of the most heavily populated areas of the deformation texture. The peripheral (111) poles are similar in each and that part of the recrystallization texture seems to be derived unchanged from the rolling texture. The central (111) poles are not reproduced with a corresponding intensity. One has mostly changed to the three possible twin positions with one particularly strong area in the rolling direction. Other areas may be partly rationalized on the basis of twinning from the peripheral (111) poles and complementary poles of the original (110) [117] orientation. Although the latter were too weak to show up in the X-ray

photographs of the as-rolled sheet, they must have been present to contribute to the new texture. The correlation of twin positions with the actual pole figure shows deviations that are partly explicable on the basis that poles of hypothetical twins have been plotted from a perfect (110) [117] orientation while the original rolled sheet showed noticeable deviations from this ideal.

The microstructure of the 85 per cent reduction specimen at an intermediate stage of recrystallization corroborates the X-ray pole-figure evidence in a general way. Fig. 18 reproduces one of the coarse, heavily twinned new grains in the lightly strain-marked structure. The directions indicated by the edges of the twin markings in Fig. 18 correspond generally to the original octahedral planes. No residual "heavy" strain markings were found at this stage of annealing. Fig. 19 shows a large grain with no twins, and it may be surmised that its orientation approaches that of the original rolled crystal, since one edge of the grain is slightly in relief while the other is scarcely discernible.

After a 95 per cent reduction, the original single crystal that exhibited both light and heavy strain markings recrystallized to form a coarse-grained structure with a strong, nonsymmetrical texture (Fig. 23). Again, the original peripheral (111) areas are reproduced with a relatively high intensity; the central (111) areas, with moderate intensity. The six twins from the center (111) poles are found and those close to the rolling direction are of high intensity. The complementary central (111) poles, which were very weak in the rolled texture, apparently have equal influence in the formation of the twinned recrystallization texture. Twins from the peripheral (111) poles again apparently contribute the strong coverages near the center of the transverse axis. In this 95 per cent reduction pole figure, additional heavily populated areas appear for the first time in sections that correspond to twinning from the central (111) poles at a (110) [112] orientation nearest the original (110) [117] position. No twins from the complement of this (110) [112] orientation appeared in the pole figure.

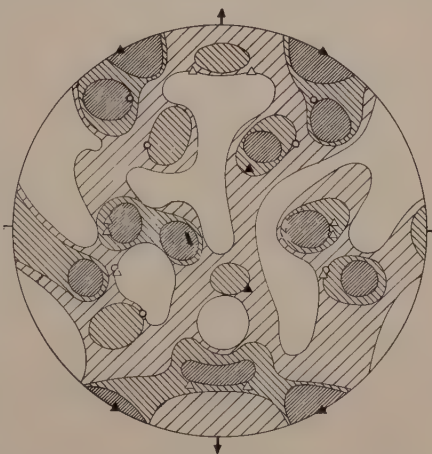


FIG. 24.—OCTAHEDRAL POLE FIGURE OF SINGLE-CRYSTAL BRASS ROLLED 99% PER CENT, ANNEALED AT 400° C.

Solid triangles, (111) poles of a (110) [113] original deformation texture. Hollow triangles, twins on central (111) poles. Dotted triangles, twins on peripheral (111) poles and complements. Circles, twins on central poles of a (110) [112] orientation.

The microstructure of the partially recrystallized 95 per cent reduction specimen showed banded areas in which recrystallization was barely initiated and the structure was predominantly light strain markings (Fig. 20). In other sections, presumably where heavy strain markings formerly existed, a fine-grained structure formed throughout a band roughly parallel to the rolling direction.

The specimen rolled to a 99 per cent reduction exhibited a recrystallization pole figure (Fig. 24) related to the deformation texture in much the same way as at the two lower reductions. The rolled texture appears strongly at the periphery, less strongly in the center and twins from residual (111) poles at the (110) [117] positions as well as from those placed according to a (110) [112] texture appear to contribute to the recrystallization structure. The texture that appeared to be symmetrical in some of the photograms is strong but nonsymmetric and does not conform to the usual (112) [113] recrystallization figure. Although the pole positions shown by twinning are not in very good accord with the actual figure, it should be recalled that the original texture was far from an exact (110) [112] orientation.

The present work on aluminum corroborated the deformation textures shown by Vargha and Wasserman.¹¹ The metal was rolled to 0.002-in. foil and X-rayed directly. The pole figures are not reproduced here but exhibited a combination of a (110) [112] and a (001) [110] texture, the latter being a surface texture, according to Vargha and Wasserman. The X-ray photograms of the aluminum exhibited considerably stronger asterism than any of the brass specimens. Is it possible that this is related to the absence of twinning in aluminum? At any rate, the recrystallization photograms did not develop the (112) [113] texture of brass but showed a weak texture similar to that of the cold-rolled foil.

SUMMARY

1. The (110) [112] texture seems to be the most stable preferred orientation for rolled polycrystalline 70-30 brass, although a considerable part of the metal shows deviations in the form of a spread, [113] to [117] in the rolling direction even at reductions of 99 per cent.

2. The reduction at which the texture becomes readily distinguishable is greatly influenced by the prior grain size of the material. A coarse-grained brass shows strong indications of a texture at a 50 per cent reduction while a very fine-grained brass may require a reduction of 90 per cent to give an equal degree of preferment.

3. The texture appears to develop by rotation of a (110) into the rolling plane with a later and usually incomplete rotation of [112] into the rolling direction. A single crystal with a single orientation of (110) [117] at a 57 per cent reduction was rolled to 95 per cent without changing its orientation and with only traces of the complementary positions appear-

ing in the deformation X-ray photograms. At a 99 per cent reduction, it partly shifted to a (110) [113] texture showing full complementary development at peripheral poles.

4. The single crystal in the (110) [117] orientation, rolled to an 85 per cent reduction, generally exhibited only regular, light transverse markings and a few others apparently parallel to octahedral poles. From 85 to 95 per cent reductions, longitudinal bands of heavy, transverse, often cellular, markings appeared and increased in quantity while the X-ray photograms at the same time showed the first traces of the complementary orientation. At the 99 per cent stage of reduction, heavy transverse markings appeared throughout the microstructure.

5. The evidence offered by the general conformation of the polycrystalline, deformation pole figures and by the correlated microstructures and pole figures of the single crystal do not tend to confirm the theory that the strain markings are mechanical twins of the dominant (110) [112] texture. The amount of metal actually in the markings is too small to greatly influence the pole figure. It seems probable that the banding that involves a considerable proportion of the metal must, in accordance with Barrett's results on aluminum and iron, be attributed to the division of a crystal into parts of differing orientations. Presumably in the rolled single crystal studied here, the strong etch markings accompany the origin of a complementary orientation.

6. The strength of the recrystallization texture appears to be a function of the degree of preferment in the original deformed structure. The usual empirically chosen description of the annealing pole figure is a (112) [113] texture. The actual texture, however, is equally well described by twins from the secondary rolled texture, approximately (110) [115], and by traces of the original primary texture.

7. The single-crystal specimens at various stages of reduction gave nonsymmetrical textures after recrystallization, which were best explained as follows:

(a) 57 per cent (*deformed*; (110) [117])—no complements—light markings)—practically random recrystallized structure.

(b) 85 per cent (*deformed*; (110) [117])—fragmentary evidence of complements—a few heavy markings)—recrystallized strongly in original orientation; twins from original positions and twins from complementary positions of nearly equal strength.

(c) 95 per cent (*deformed*; (110) [117])—traces of complements—numerous heavy markings)—recrystallized strongly in original orientation; twins from original positions and equally strongly, from their complements; twins from the single (110) [112] nearest the original orientation, but not its complement.

(d) 99 per cent (*deformed*; (110) [113] + (110) [117])—complements nearly complete—heavy markings)—recrystallized strongly in original orientations; twins from (111) poles in both of original textures.

8. It is believed the evidence indicates that in general the recrystallization texture is derived from the deformation texture by twinning on (111) poles and by new grains in the original (110) [112] orientation. The poles most active in the twinning action appear to be those in the central part of the pole figure oriented according to the usual polycrystalline secondary texture, (110) [115]. The strong presence of annealing twins from complementary orientations of the single crystals that were not visible in the cold-rolled texture and from the (110) [112] texture in the single crystal when only the (110) [117] was noticeable in the rolled state indicates the pole-figure method is insensitive to relatively minute proportions of metal in the rolled sheet. It is quite possible the strain markings are the site of mechanical twins that form the nuclei for subsequent annealing twins and the correlated recrystallization textures, but the evidence must be considered only as suggestive.

ACKNOWLEDGMENT

The author is indebted to Prof. C. H. Mathewson for many helpful discussions in the course of this work.

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DISCUSSION

(L. W. Eastwood presiding)

G. SACHS,* Cleveland, Ohio.—Were the photomicrographs taken on the same specimens that were used for the X-ray investigations? Is it possible to describe

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the recrystallization structure of brass as consisting of the same fundamental orientations as the rolling structure but in different intensities?

C. S. BARRETT,* Pittsburgh, Pa.—While I do not share the author's enthusiasm for the twinning theory he is attempting to test here, I should like to suggest a different kind of twinning relation that should be considered; that is, a twinning relation between different grains of the recrystallized metal. In aluminum after compression and recrystallization some of the grains are twins of their neighbors, although none seem to be twins of the deformed matrix. Also, in recrystallized iron, Mr. Levenson and I have found twin orientations between large crystals and small grains that had not been absorbed during recrystallization.

It is interesting to compare the textures of rolled and of recrystallized brass with the textures of brass after compression. I have found the compression texture of 70-30 brass to have strong [110] and weak [111] components, and to differ from copper, in which the [111] texture is absent. This double compression texture of brass was not changed by recrystallization. Fig. 4 shows a [111] component in the "compression direction," normal to the sheet, in agreement with the compression texture. An earlier pole figure of Wever's for rolled brass failed to show this. This component seems to be missing after recrystallization (Fig. 21).

R. M. BRICK (author's reply).—The photomicrographs were taken at an intermediate stage in the recrystallization process and the X-ray investigation made of similar specimens but after recrystallization was complete. The recrystallization texture does consist in part of the same fundamental orientations as the rolling structure but several marked differences appear (Figs. 4 and 21), which seem to be best rationalized on the basis of twinning.

The author deprecates any appearance of enthusiasm for the twinning theory, although it must be admitted that after obtaining the pole figures reproduced in the paper and failing to correlate them on the basis of any prior hypothesis, it was rather pleasant to find that they might be rationalized by twinning from the secondary deformation textures. An alternative and superior explanation would be welcome. Application to rolled brass of Dr. Barrett's method of determining localized orientations by etch-pit methods might support his suggestion of a twinning relation between different grains. This correlation found in iron and aluminum should not necessarily be expected in brass, since the former metals rarely show the internal annealing twins that are so abundant, one might say predominant, in worked and annealed brass.

No explanation occurs to the author for the absence of the weak {111} component of the rolling texture in the recrystallization pole figure. It is interesting that Dr. Barrett found this weak component present in both deformed and recrystallized compression specimens. The absence of the {111} texture in Wever's pole figure for rolled brass might be occasioned by a different relation between roll diameter and specimen thickness, with a resultant different compression component during the deformation.

R. F. MEHL, discussion on page 168.

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Tensile Deformation of Critically Oriented Brass Crystals

BY H. L. BURGHOFF,* MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

DURING the course of preparation of crystals of alpha brass for an investigation of their creep characteristics, a number of critically oriented crystals were produced. In each of these specimens, P_0 , the specimen axis, lay near some important crystallographic direction or on or near the border of two possible slip systems. Because of the unusual nature of their orientations, it was considered of interest to deform these specimens in simple tension and to study orientation changes and any unusual occurrences, different from what would be expected for specimens in which only one slip system had distinctly the highest maximum resolved shear stress.

Choice of actual operating slip system in a crystal offering an immediate possibility of two slip systems would be expected to be due to chance, defect, or some inhomogeneity. Even in an ideally perfect crystal so oriented, the natural oscillations of the atoms about their lattice positions would give rise to a condition wherein one slip system would be favored over the other at the critical shear stress. In the large, nonperfect crystals of the present investigation, slip on both systems, but in different portions of the specimen, might occasionally be expected.

DETERMINATION OF ORIENTATION AND OPERATING SLIP SYSTEM

Orientations of specimens before and after deformation were determined by Greninger's back-reflection Laue method.¹

Elam² has shown that deformation of alpha brass crystals proceeds as with crystals of aluminum and of copper; that is, the slip plane is a $\{111\}$ plane and the slip direction is a $\langle 110 \rangle$ direction. There are, however, four possible slip planes of $\{111\}$ form and each plane has three possible slip directions, so that there is a total of 12 possible slip systems in a face-centered cubic lattice. It is evident that the system for which the tangential component of shear is maximum will function

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¹ References are at the end of the paper.

as the slip system, and this tangential component of shear is given by Elam³ to be:

$$S = \frac{P}{A} \sin X \cos \lambda$$

where S = resolved shear stress; P , applied load; A , area of cross section of specimen; X , angle between $\{111\}$ and specimen axis; λ , angle between $\langle 110 \rangle$ and specimen axis.

It is thus possible to predict the slip plane and direction of slip of any crystal whose orientation is known, and Taylor and Elam⁴ have shown how a stereographic figure can be obtained in which a point P , represent-

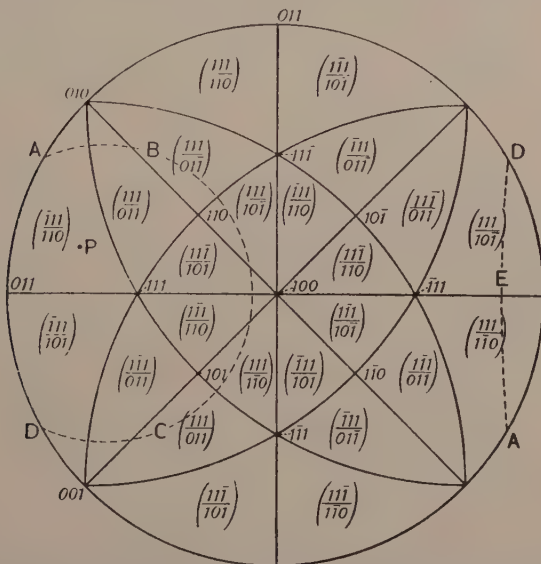


FIG. 1.—STEREOGRAPHIC DIAGRAM FOR PREDICTION OF SLIP-PLANE AND DIRECTION OF SLIP FROM KNOWLEDGE OF ORIENTATION OF CRYSTAL.⁴

ing the axis of the specimen (cubic crystal), can be put into one of 24 similar spherical triangles; and that P always falls into the same triangle by suitable choice of the $\langle 100 \rangle$ axis to rotate into the center. They have also shown that if the axis P lies in a particular triangle it will deform by slip on one particular plane and in one particular direction, and have accordingly developed the diagram shown in Fig. 1, which gives the slip plane and slip direction for each triangle.

This method of analysis was used in the present investigation, so that calculation of maximum resolved shear stress for the operating slip system was a simple matter in a crystal of known orientation.

TEST MATERIALS AND EXPERIMENTAL WORK

The crystals were made by the Bridgman method⁵ in the form of rods $\frac{1}{2}$ in. in diameter and about 9 or 10 in. long, high-grade 70-30 brass being

used as raw material, with the finished crystals containing approximately 71 per cent Cu. In preparation for testing, the specimens were carefully machined to a diameter of about 0.450 in. for a gauge length greater than 6 in., annealed for 16 hr. at 1350°F. to reduce coring, and then cleaned or etched in nitric acid solution. Extension of the specimens was accomplished in an Amsler hydraulic testing machine of 20,000 lb. capacity, the 2000-lb. range being used for proper sensitivity, and Templin grips being employed to ensure axial loading.

After test, each specimen was again submitted to X-ray analysis, to determine change in orientation due to the deformation experienced and also to establish the crystallographic significance of slip markings when observed. The theoretical final position of the specimen axis (final orientation) was also plotted for comparison with the position actually observed, the calculation being made from Schmid and Boas' formula:⁶

$$\sin X_1 = \sin X_0 \frac{l_0}{l_1}$$

where X_1 = final angle between slip plane {111} and specimen axis,

X_0 = original angle between slip plane {111} and specimen axis,

l_0 = original length of specimen = 1,

l_1 = final length of specimen = 1 + total elongation.

Knowing the angle between the slip plane and the final position of the specimen axis, and the course of movement of the specimen axis on the stereographic projection according to the Taylor and Elam theory, the theoretical position is readily plotted.

TABLE 1.—*Data and Test Results for Critically Oriented Crystals*

Specimen No.....	14-2	31-1	12-1	29-1
$X_0(P \wedge \{111\})$	33°	53°	28°	47°
$\lambda_0(P \wedge \langle 101 \rangle)$	43°	58½°	30°	48°
$\sin X_0$	0.544	0.798	0.469	0.731
$\cos \lambda_0$	0.731	0.522	0.866	0.669
$\sin X_0 \cos \lambda_0$	0.397	0.416	0.406	0.489
Critical resolved shear stress, grams per sq. mm...	1440	1400	1370	1395
Total extension, per cent.....	7	7	38	13

The orientation data for this group of specimens are summarized in Table 1, which also includes some test results, the peculiarities of the orientations being as follows:

14-2, in which P_0 lay on the great circle passing through the poles of the (011) and (111) planes, giving two slip systems of equal maximum resolved shear stress having a common slip plane but different slip directions.

31-1, in which P_0 lay very close to the pole of the (011) plane so that four slip systems of approximately equal resolved shear stress existed.

12-1, perhaps the most interesting fundamentally, in which the specimen axis P_0 coincided, within the limit of error of determination, with the pole of the (112) plane, the orientation approached as a final position for such face-centered cubic crystals when deformed in simple tension; there were two slip systems having maximum resolved stress and double or alternate slip was possible.

29-1, in which P_0 lay very close to the great circle through the poles of the (101) and (001) planes, so that there were two slip systems of approximately equal maximum resolved shear stress involving different slip planes and slip directions, the action of slip on one system tending to reduce resolved stress on the other.

RESULTS

Specimen 14-2.—Specimen 14-2 was extended a total of 7 per cent, and deformation took place by slip on one system only. Critical resolved shear stress was 1440 grams per sq. mm., the load dropping very slightly at the initiation of plastic deformation and thereafter rising steadily to a maximum resolved shear stress of 1615 grams per sq. mm., based upon the original orientation, at the end of the extension. Deformation was definitely progressive, as slip markings first appeared in the lower part of the 6-in. gauge length and spread upward as extension proceeded. Although total elongation was 7 per cent, actual elongation along the specimen was distinctly variable, elongations in successive 1-in. intervals from bottom to top being 12, 11, 9, 6, 2.5 and 1 per cent, respectively. Orientation change was measured by X-ray means, the extension of the specimen at the point of incidence of beam being about 10 per cent. The movement of the specimen axis is shown in Fig. 2, and is as predicted for slip on one system.

Specimen 31-1.—Specimen 31-1 was also extended 7 per cent, and deformation took place by slip on one system only. As for specimen 14-2, slip was progressive and not uniform throughout the 6-in. gauge length, elongation in successive 1-in. intervals from bottom to top being: 9, 9, 9, 6, 7 and 2.5 per cent. Resolved shear stress as plastic deformation first began was 1400 grams per sq. mm. This decreased to 1325 grams per sq. mm. during the first plastic extension and then rose steadily to 1430 grams per sq. mm. at the end of the extension. Orientation change is shown in Fig. 2 for a section elongated 9 per cent, and is as expected for slip on one system.

Specimen 12-1.—Specimen 12-1 was examined after successive extensions to 1, 5, 15, 30 and 38 per cent total elongation in the original 6-in. gauge length. As explained before, the axis of this specimen originally

coincided with the pole of the (112) plane within the limit of error of determination; that is, within about one degree.

Critical resolved shear stress was 1370 grams per sq. mm., and a definite yield point was observed, being evidenced by a very slight decrease in load during the first plastic extension. Load thereafter continually increased throughout the tests as extension proceeded and normal tensile stress attained a value of 13,000 grams per sq. mm. for 38 per cent elongation, at which time extension was stopped for further examination of the specimen. When pulled to fracture at a later date, the maximum normal tensile attained was 15,000 grams per sq. mm. and elongation in 2 in. was 100 per cent. Incidentally, this specimen was not as ductile,

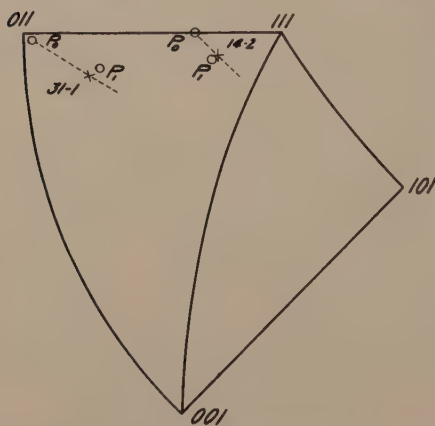


FIG. 2.

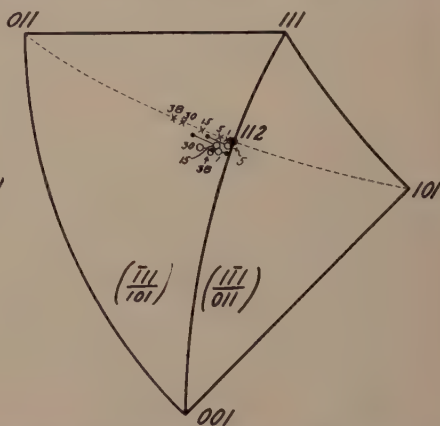


FIG. 3.

FIG. 2.—DIAGRAM SHOWING ORIENTATION CHANGES FOR SPECIMENS 14-2 AND 13-1.

Circle shows observed position of specimen axis P .

Cross shows position calculated for observed extension.

FIG. 3.—DIAGRAM SHOWING POSITIONS OF AXIS OF SPECIMEN 12-1 AFTER 1, 5, 15, 30 AND 38 PER CENT EXTENSION. ORIGINAL POSITION COINCIDES WITH POLE OF (112) PLANE.

Cross indicates theoretical position of axis for observed extension, assuming movement on (111) only and in (011) direction.

Circle indicates observed position of axis for percentage elongation shown.

Dot indicates theoretical position calculated for movement on one plane only from previous observed position.

evidently because of the original orientation, as a specimen for which P_0 lay well within the stereographic triangle and which elongated 175 per cent when pulled to fracture. Elam has also reported elongations as high as 168 per cent for brass crystals of the same composition.

The orientation changes for the various steps are shown in Fig. 3. The points, designated by x and lying on the great circle passing through P_0 , or pole of the (112) plane, and the pole of the (011) plane, are the calculated positions that should result from slip on the plane ($\bar{1}\bar{1}1$) in the [011] direction for the various increments of extension. Actually none of these positions was realized, but it did appear that slip began on the ($\bar{1}\bar{1}1$) plane, as will be explained in more detail.

For the initial 1 per cent extension the apparent slip plane, as evidenced from slip markings and X-ray analysis, was the $(\bar{1}\bar{1}1)$ plane. The calculated and observed positions of P_1 per cent did not agree very well, but the angle between P_1 per cent and $(\bar{1}\bar{1}1)$ was the same for both, and P moved away from the stereographic triangle

$\begin{pmatrix} \bar{1}\bar{1}1 \\ 011 \end{pmatrix}$ as would be expected for slip on $(\bar{1}\bar{1}1)$.

Therefore it would appear that this 1 per cent extension took place by slip on the $(\bar{1}\bar{1}1)$ plane.

For 5 per cent total extension, P_5 per cent was even closer to the pole of the (112) plane or P_0 than was P_1 per cent. Even though only the original set of slip markings was visible, the extension from 1 to 5 per cent apparently did not take place by slip on $(\bar{1}\bar{1}1)$, for P_5 per cent moved in the opposite direction, somewhat toward $[101]$, indicating slip on $(\bar{1}11)$. Using P_1 per cent as observed for the starting position of the 1 to 5 per cent movement, and assuming slip on $(\bar{1}11)$, P_5 per cent as observed does not coincide with the calculated position, but both positions give about the same angle between $(\bar{1}11)$ and P .

For 15 per cent total extension, P moved from P_5 per cent toward the pole of the (011) plane, indicating slip on $(\bar{1}\bar{1}1)$, and the slip markings corresponding to this plane were still the ones evident. However, the observed position of P_{15} per cent was considerably short of the position expected from slip solely on $(\bar{1}\bar{1}1)$. It would appear, therefore, that there was some minor slip upon $(\bar{1}11)$ in this interval.

For 30 per cent total extension, P moved from P_{15} per cent somewhat toward the pole of the (011) plane, again indicating slip on $(\bar{1}\bar{1}1)$. Here again the observed position of P_{30} per cent was short of the position expected from slip only on $(\bar{1}\bar{1}1)$ for this amount of elongation. Some slip therefore was indicated to have taken place on $(\bar{1}11)$, and, in fact, a number of slip markings corresponding to this latter slip plane appeared during this interval.

When the specimen was finally stretched from 30 to 38 per cent elongation, the axis P moved back from P_{30} per cent toward the pole of the (101) plane, indicating slip on $(\bar{1}11)$. As the markings corresponding to this plane actually increased greatly in number, and the observed and calculated positions of P_{38} per cent practically coincided, it appeared that all the slip in this interval was on the $(\bar{1}11)$ plane.

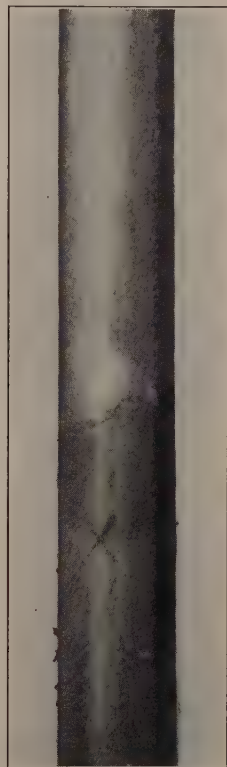


FIG. 4.—APPEARANCE OF PORTION OF SPECIMEN 29-1 AFTER 13 PER CENT EXTENSION. $\times 1\frac{1}{2}$.

Slip markings are visible in both upper and lower zones and in transition zone.

After completion of the tests on this specimen, the second set of slip markings was readily visible while the original set was almost obliterated. It is to be mentioned that extension or deformation was uniform throughout the gauge length at each stage.

To summarize the work on this specimen, it appeared that the supposedly stable original orientation was not maintained. Deformation began by slip on one of the two planes of maximum resolved shear stress

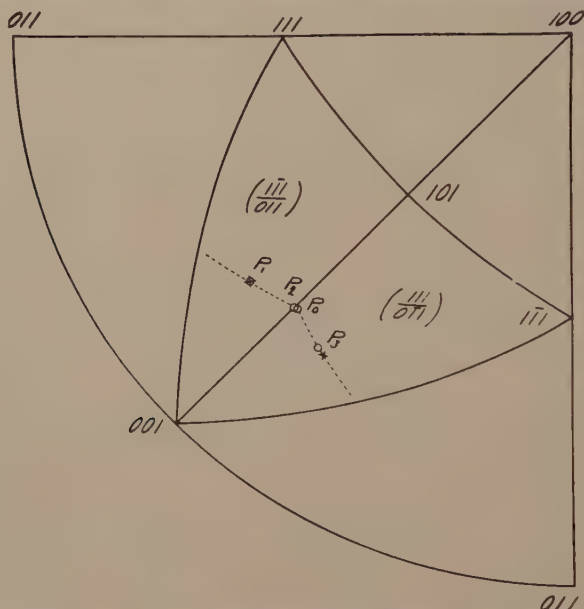


FIG. 5.—POSITIONS OF AXIS OF SPECIMEN 29-1 BEFORE AND AFTER 13 PER CENT EXTENSION.

P_0 is original position; P_1 is final position for upper zone; P_2 , final position for transition zone; P_3 , final position for lower zone.

Circle is observed position; cross, position calculated for observed extension.

and later proceeded by double or alternate slip on both these planes. Non-uniform hardening of these two slip planes was indicated as has been found in other work on brass crystals where double or alternate slip was possible. During the last stage of the deformation the specimen axis again approached the initial orientation.

Specimen 29-1.—Specimen 29-1, the axis of which lay very close to the great circle passing through the poles of the (101) and (001) planes, was elongated 13 per cent, and maximum resolved shear stress was 1395 grams per sq. mm. as plastic deformation first started. A small but definite decrease in load was observed during the first plastic deformation, the “upper yield point” corresponding to a resolved stress of 1430 grams per sq. mm. and the “lower yield point” to 1405 grams per sq. mm. Resolved stress then increased steadily to 1620 grams per sq. mm. at 13 per cent elongation.

Deformation occurred quite uniformly throughout the 6-in. gauge length, but did not take place by slip on one system only. Rather, slip began simultaneously in different parts of the specimen on both systems of maximum resolved shear stress, so that three distinct zones resulted. The first or central zone slipped on one system while the two adjacent zones slipped on the second system. Where these zones merged, transition appeared to be effected with the assistance of bend planes. Elongation in these transition zones was lower than the average for the specimen, actual elongations in successive 1-in. intervals from top to bottom being as follows: 11 per cent, 12 per cent, 13 per cent, 14 per cent, 11 per cent and 14 per cent. The transition zones occurred in the intervals of 11 per cent elongation, a greater resistance to slip thus being evident in these complex regions. It was noted that some slip bands of the two functioning systems definitely overlapped in the transition zones, so that a special case of double or alternate slip existed. Fig. 4 shows the appearance of the lower transition section and the adjacent portions of the specimen.

Orientations in the lower transition zone and the adjacent regions of one-system slip were investigated. Fig. 5 shows the results of the X-ray analysis, and it is seen that the two regions of one-system slip change orientations as expected and are quite symmetrical with respect to the transition zone, which, in spite of obvious deformation, retained the original orientation very closely, the axis lying exactly on the great circle passing through the pole of the (001) and (101) planes.

SUMMARY

The deformation of these four critically oriented crystals in short-time tension tests provided a demonstration of the applicability of the law of maximum resolved shear stress with deformation possible on different slip systems in adjacent regions of a crystal at the same time. Movement of the axis of a specimen about its original and supposedly stable position, which corresponded to that of the pole of the (112) plane, was shown. In addition, each specimen was found to have an "upper" and a "lower" yield point in these short-time tests.

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Recrystallization of Lead

By PAUL A. BECK,* MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

WHILE the recrystallization properties of most of the practically important metals are known in considerable detail, those of lead are still relatively little known in spite of some valuable contributions in recent years. This condition probably is due to the difficulties involved in applying the usual methods of investigation.

The microscopic method of discriminating between the elongated deformed grains of the familiar lenticular shape and the equiaxed recrystallized grains is not successful with fully refined lead: lenticular grains cannot be seen under the microscope with any amount of deformation whatever. The probable cause of this phenomenon was recognized long ago. With large deformation the time of recrystallization at room temperature is shorter than the period of preparation of the specimen for microscopic examination; with small deformation the deformed grains are not noticeably elongated in the first place. However, with small deformation the migration of the grain boundaries can be observed. The only systematic investigations yet published on the recrystallization of lead, those by R. S. Russell,¹⁻³ make use of the conditions just described. Russell considered recrystallization completed when no further migration of boundaries could be observed. A serious objection to this method arises from the fact that there is no evidence to support the view that grain-boundary migration results *only* from recrystallization. If such migration does result from other sources after recrystallization is completed—after the deformed grains have been replaced by new undeformed grains—the “time of recrystallization” as determined by Russell may be too long. Furthermore, the method is subject to the above-mentioned limitation because of the unavoidable period of preparation of the sample. According to Russell, even with the fastest technique 5 min. elapsed before the deformed samples were ready for examination, and consequently no recrystallization time shorter than 5 min. could be measured.

The lack of success in detecting the recrystallization of lead by the usual hardness or tensile tests is again caused by the time necessary for

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¹ References are at the end of the paper.

the performance of such tests. If the deformation is large enough to produce considerable hardening, recrystallization takes place so fast that the metal cannot be tested in the cold-worked condition; if the deformation is small, the resulting hardening is too small to be detected.

In order to avoid these difficulties, a different method was used in the present investigation. It is well known that the grain size produced by recrystallization due to deformation and subsequent annealing depends on the degree of deformation. In using a certain constant time and temperature of annealing, there will be a more or less definite lower limit of deformation, below which no recrystallization takes place and the grain size remains unchanged. If the deformation is somewhat higher than this critical value (a in Fig. 1), very large new grains result (critical recrystallization). Further increase in the deformation yields continuously decreasing grain sizes.⁴ The critical deformation, of course, is not a constant for the material used, since it also depends on the time and temperature of annealing. Generally, if the temperature of annealing is high enough, approximately 1 or 2 per cent elongation will cause critical recrystallization; viz., the formation of grains up to 1000 times larger than the original ones. It is clear, however, that this is true only for initially strain-free material, or for that which has been less than critically strained

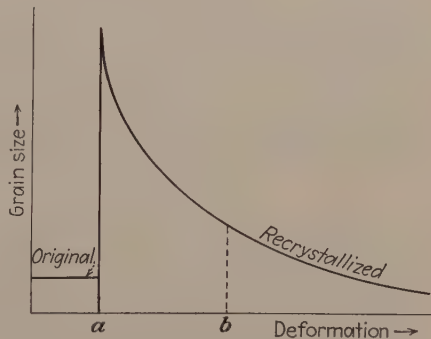


FIG. 1.—GRAIN SIZE AS FUNCTION OF DEFORMATION FOR GIVEN TIME AND TEMPERATURE OF ANNEALING.

previously. If the additional strain of 1 or 2 per cent is applied to a material initially deformed to a larger extent (b in Fig. 1), the additional strain will have no visible effect other than *decreasing* the resulting grain size. Thus the application of a slight deformation and of subsequent annealing may be used as a test to determine whether the material was deformed or strain-free—i.e., recrystallized—at the moment when the slight deformation of the test was applied to it.⁵ Since this test deformation can be performed very quickly, the method permits measuring time of recrystallization of less than one minute.

METHOD OF TESTING

The method of testing as actually used in the present investigation consisted in the application, at adequate intervals, of indentations with the aid of a simple 7-in. cut nipper, and in subsequent annealing. Since all indentations were made along one edge of the strip to be tested, they produced some bending. The strip was slightly elongated near the

indented edge, and slightly compressed at the other edge. After annealing the surface of the specimens was etched in a mixture of 1 part hydrogen peroxide solution (35 per cent), 2 parts glacial acetic acid and 3 parts water. Fig. 2 shows the etched surface of a specimen with no critical recrystallization; evidently the strip had not yet recrystallized when the indentations were made. The specimen of Fig. 3 is another piece of the same strip, which, however, was indented only 16 min. after rolling.

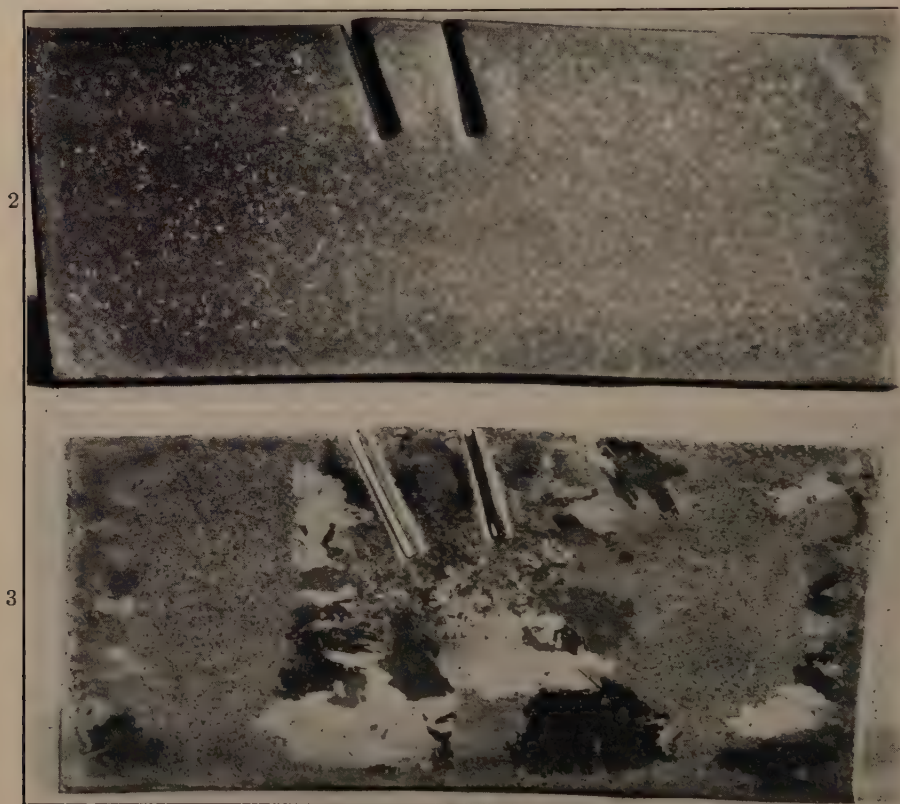


FIG. 2.—ROLLED SAMPLE, INDENTED BEFORE RECRYSTALLIZATION, THEN ANNEALED AND ETCHED.

FIG. 3.—ROLLED SAMPLE, INDENTED AFTER RECRYSTALLIZATION, THEN ANNEALED AND ETCHED.

The well-developed critical recrystallization shows that the recrystallization was practically complete when the indentations were made.

With some practice it was found possible to execute the first indentations within 5 sec. after the strip left the rolls. Further indentations were usually made at 15, 30, 45 sec., 1, 1.5, 2, 2.5, 3, 5 min., and so forth at increasing intervals.

In order to correlate the results obtained by the critical recrystallization method to those obtained by hardness measurements, a check

experiment was carried out under conditions that permitted the application of Brinell tests. A bar of cast tellurium lead, containing 0.084 per cent Te, was cold-rolled in 10 per cent passes from 0.75 to 0.1 in. Two adjacent parts of this strip were used; one for the Brinell tests, the other for the critical recrystallization tests. As recrystallization of this lead at room temperature is slow, an annealing temperature of 100° C. was used. The two specimens were annealed together in an automatically controlled electric oven, and removed from the oven at adequate intervals for testing. For each test the specimens were removed from the oven together, placed on a heavy steel plate, and tested after attaining room temperature. After testing they were replaced in the oven together. Two impressions were made for each Brinell test, using a 10-mm. ball, 30 sec. time, and a dead load of 100 kg. Two measurements of diameters at right angles were made of each impression, so that four values were obtained for each point. Of these the highest and the lowest were recorded. After a total annealing period of 5.5 hr., the last Brinell impressions and indentations were made, and the indented specimen was annealed 1 hr. at 210° C. for critical recrystallization. Table 1 gives the Brinell hardness number and the presence or absence of critical recrystallization after various periods of annealing at 100° C. These data are

TABLE 1.—*Critical Recrystallization*

Period of Annealing	Brinell Hardness	Critical Recrystallization
Minutes		
0	8.3-8.5	None
3	8-8.5	None
10	8-8.5	None
17	8-8.5	None
25	8	None
35	7.8-8.3	None
45	7.6-8	None
65	7.2-7.6	Traces
95	6.9-7.4	Beginning
Hours		
2.5	6.4-6.6	Complete
5.5	6-6.2	Complete

shown in Fig. 4. The dotted vertical line represents the first appearance of complete critical recrystallization, which, as readily seen, coincides with the end of the major hardness drop. Thus the check experiment confirms that critical recrystallization in the indented samples is indicative of the practical completion of recrystallization at the time when the indentation was made.

It has been observed, in the course of this work, that the surfaces of the specimens were often rough in the neighborhood of the indentations.

Closer examination revealed that this roughness depended on the internal condition of the material when the indentation was made. As rolled, the strips were very smooth, as shown by the uniformly high light reflection of the surface. If the indentations were made soon after rolling, while the material was still hard, a narrow band of roughness appeared at the end of each indentation. In these bands the little hills and valleys were close together. Their average "wave length" and average "amplitude" were small. However, indentations made on partially recrystallized material caused the formation of much wider bands, in which, superimposed on the fine "waves" described above, larger areas of protrusions and recessions were found. When recrystallization was completed these formations of longer "wave length" did not appear, and only the finer "waves," similar to those formed in completely hard material, were seen.

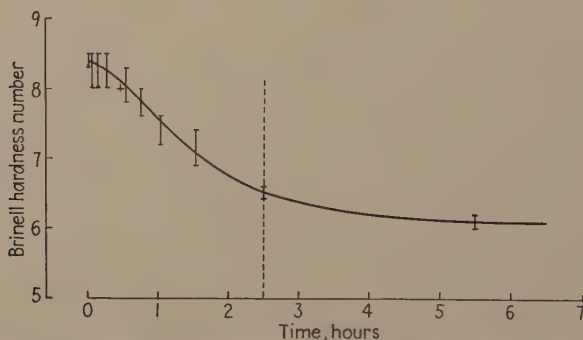


FIG. 4.—BRINELL HARDNESS AS FUNCTION OF PERIOD OF ANNEALING AT 100° C. OF ROLLED TELLURIUM LEAD.

The width of the bands increased continuously from hard to soft material. These three characteristic stages are shown in Figs. 5, 6 and 7.

The phenomena described can be readily interpreted as follows: The fine waves are due to orientation difference between the neighboring grains, and to the corresponding differences in the slip directions. The long waves, found in partially recrystallized material, correspond to adjacent hard and soft areas. It was possible to use the appearance of the long waves as an indication that recrystallization is proceeding and their more or less gradual disappearance as an approximate indication of completed recrystallization. The indications obtained by this method of "deformation figures" usually checked fairly well with the results of the more accurate critical recrystallization method, and served as useful guides in the appropriate timing of the indentations.

After the deformation figures indicated that the recrystallization was complete, the test was usually continued for some time, and the samples were then annealed for 1 hr. at 150° C. This annealing was not necessary for high-purity lead, where critical recrystallization readily took

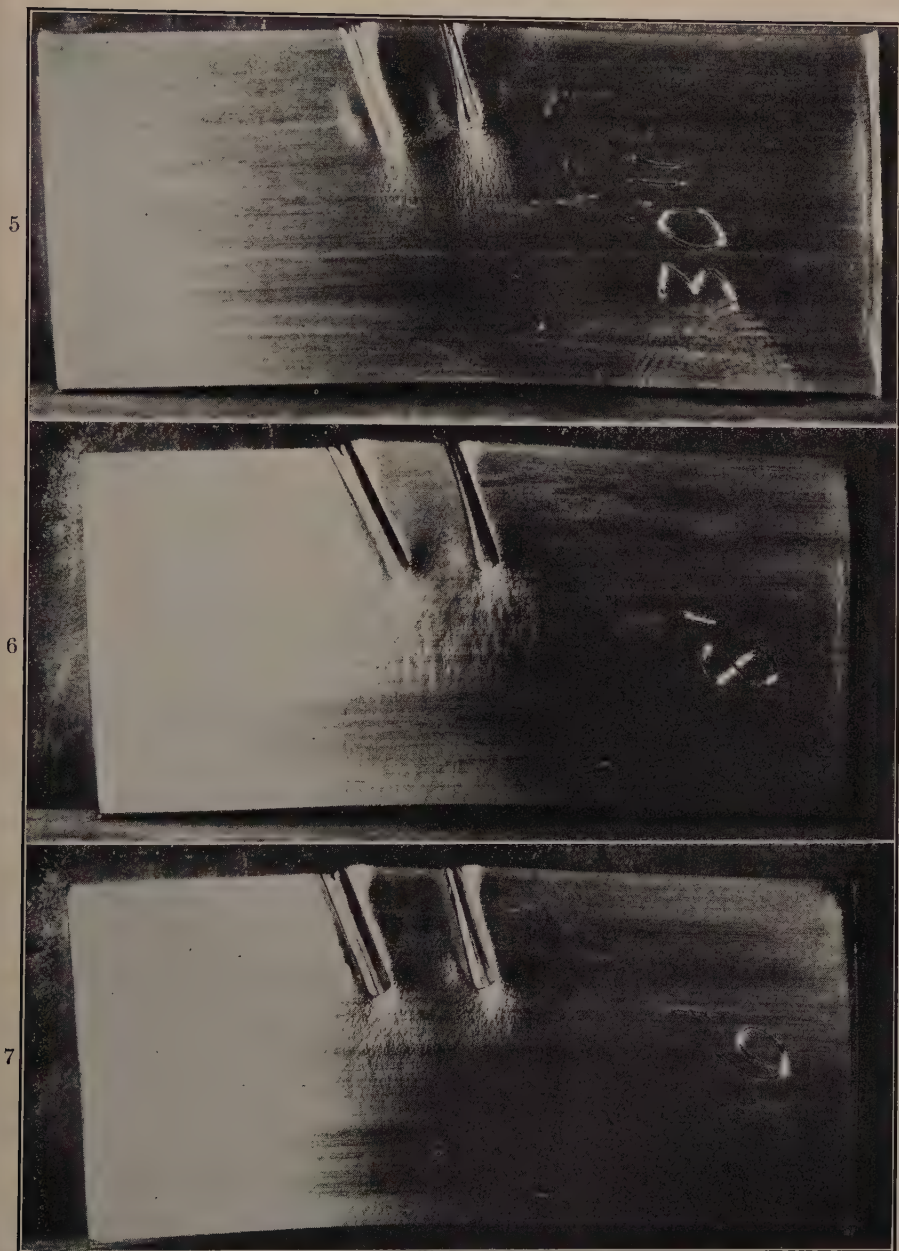


FIG. 5.—ROLLED SAMPLE, INDENTED BEFORE IT RECRYSTALLIZED.

FIG. 6.—ROLLED SAMPLE, INDENTED WHEN PARTLY RECRYSTALLIZED.

FIG. 7.—ROLLED SAMPLE, INDENTED AFTER IT RECRYSTALLIZED.

place at room temperature and was complete in a few hours. Subsequent annealing at 150° C. did not cause further noticeable change.

The time of recrystallization of the following leads was investigated: high-purity lead, common lead, acid lead, and silver lead. The high-purity lead was produced by a special refining procedure at the Central Research Laboratory of the American Smelting and Refining Co. Spectrographic and chemical analyses proved it to be at least 99.999 per cent

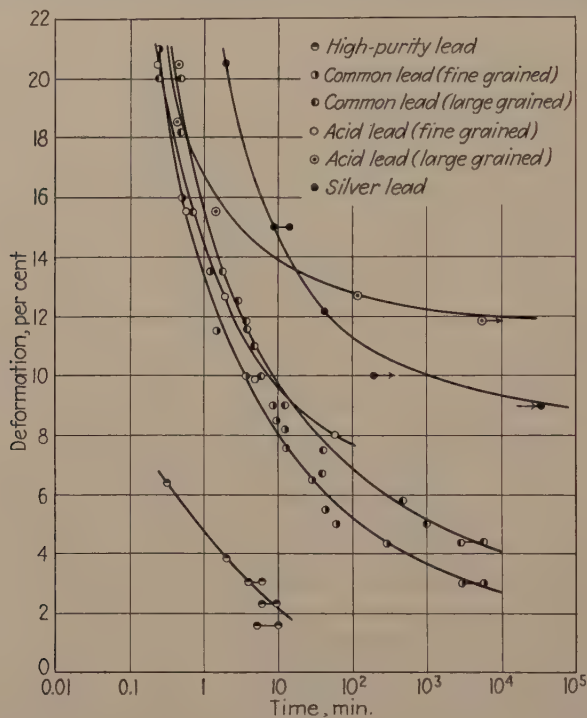


FIG. 8.—TIME OF RECRYSTALLIZATION AT 25° C. AS FUNCTION OF DEFORMATION.

pure. The silver lead was made of this high-purity lead by the addition of 0.0084 per cent fine silver. The common lead and acid lead used were produced at the Perth Amboy plant of the American Smelting and Refining Co. Their typical analyses are listed in Table 2.

All of the leads named were melted in an open graphite crucible and cast at 400° C. into an iron mold preheated to 100° C. The cast bars, measuring $\frac{3}{4}$ by 1 by 8 in., were cold-rolled in 0.04-in. passes down to 0.354 in., and in 10 per cent passes down to 0.1 in. in thickness. The period between passes was 45 to 60 sec. Strips of common lead and of acid lead were also prepared by a modified method of rolling, in which the 10 per cent passes were replaced by a correspondingly smaller number of 30 per cent passes, so that the same final thickness of the strips was secured. The time of recrystallization of the various strips was then

TABLE 2.—*Typical Analyses*
PERCENTAGES

Constituent	High-purity Lead	Silver Lead	Common Lead	Acid Lead
Cu.....	0.0000	0.0002	0.0004	0.064
Ag.....	0.0000	0.0084	0.0007	0.0007
Bi.....	0.0000	0.0000	0.1	0.020
Fe.....	0.0001	0.0001	0.0001	0.0001
Zn.....	0.0000	0.0000	0.0002	0.0002
As + Sn.....	0.0000	0.0000	0.0000	0.0000
Sb.....	0.0000	0.0000	0.0001	0.0001

determined in a set of preliminary experiments. The results, together with the resulting grain sizes, are given in Table 3.

TABLE 3.—*Results of Cold-rolling*

Specimen	Reduction per Pass, Per Cent	Time of Recrystallization	Grain Size, Mm.
High-purity lead.....	10	5 sec.	0.6
Common lead.....	10	1.5 min.	0.2-0.3
Common lead.....	30	15 sec.	0.1-0.15
Acid lead.....	10	1-2 min.	0.2
Acid lead.....	30	5 sec.	0.1
Silver-lead alloy.....	10	30 min.	0.3

After allowing enough time for complete recrystallization, the strips were given a final pass through the rolls, and the time of recrystallization was determined, for the six sets of specimens listed in Table 3, as a function of the reduction in the final pass.

RESULTS AND DISCUSSION OF RESULTS

Table 4 gives the time of recrystallization at room temperature (about 25° C.) as a function of the reduction in one pass for the six sets of specimens listed in Table 3. The information given in Table 4 is presented graphically in Fig. 8.

As seen from Fig. 8, the time of recrystallization of all leads investigated increases more than exponentially with decreasing deformation. This increase is particularly rapid for silver-lead alloy around 10 per cent deformation, and for coarse-grained acid lead at around 13 per cent deformation. For both kinds of lead in this region the deformation figures failed to give reliable results. According to the deformation figures, the recrystallization was complete much faster than indicated by the more reliable critical recrystallization method. Apart from this discrepancy the two methods checked fairly well.

TABLE 4.—*Time of Recrystallization at Room Temperature as Function of Reduction in One Pass*

Reduction, Per Cent	Time of Recrystallization		Resulting Grain Size, Mm.
	By Deformation Figures	By Critical Recrystallization	
HIGH-PURITY LEAD (GRAIN SIZE 0.6 MM.)			
1.6	5-10 min.	5-10 min.	2.5
2.3	4-6 min.	6-9 min.	2.5
3	3 min.	4-6 min.	2.5
3.8	1-2 min.	2 min.	2
6.4	25-35 sec.	25-35 sec.	0.8
FINER-GRAINED COMMON LEAD (GRAIN SIZE 0.1 TO 0.15 MM.)			
3	2-4 days	2-4 days	2
4.3	1-2.5 hr.	5.5 hr.	1.5
5	65 min.	65 min.	0.3
5.5	25-45 min.	45 min.	
6.6	64 min.	30 min.	
7.5		13 min.	
8.2	12 min.	12 min.	0.3
8.5		10 min.	
9	9 min.	9 min.	
10	4 min.	4 min.	0.2
11.5	2 min.	1.5 min.	0.15
13	1.5 min.	1.25 min.	0.15
16	30-45 sec.	30 sec.	0.1
21	15-25 sec.	15 sec.	
LARGER-GRAINED COMMON LEAD (GRAIN SIZE 0.2 TO 0.3 MM.)			
4.4	2 days	2-4 days	
5	18 hr.	18 hr.	0.5
5.8	10 hr.	10 hr.	0.3
6.75	41-90 min.	41 min.	0.3
7.5	30 min.	45 min.	
9	12-20 min.	12 min.	
10		6 min.	0.4
11	5 min.	5 min.	0.2-0.3
11		5 min.	
11.8	4 min.	4 min.	
11.6	4 min.	4 min.	
12.5	3-5 min.	3 min.	
13.5	2 min.	105 sec.	
15.6	45 sec.	45 sec.	0.2
18.2	45-55 sec.	30 sec.	0.1-0.2
20	15-25 sec.	15-25 sec.	0.1

TABLE 4.—(Continued)
FINE-GRAINED (0.05 TO 0.1 MM.) ACID LEAD

Reduction, Per Cent	No Recrystallization	First Local Recrystallization	Complete Recrystallization
5.5	1 day	3 days	
6.7	25 min.	40 min.	
8	14 min.	16 min.	1-hr.
9.9	2 min.	3 min.	3 or 5 min.
12.7	1.5 min.		2 min.
15.6	10 sec.	20 sec.	40 sec.
20.5		5 sec.	15 sec.
30			Less than 5 sec.

LARGER-GRAINED (0.2 MM.) ACID LEAD

6.7	12 days	?	?
8	12 days	?	?
9.9	18 hr.	26 hr.	More than 8 days
10.8	1.5 hr.	5 hr.	More than 4 days
11.8	12 min.	15 min.	More than 4 days
12.7	6 min.	8 min.	2 hr.
15.6	30 sec.	1 min.	1.5 min.
18.6	5 sec.	15 sec.	25 sec.
20.5		5 sec.	30 sec.
30			Less than 5 sec.

SILVER-LEAD (GRAIN SIZE 0.3 MM.)

	Time of Recrystallization		Resulting Grain Size, Mm.
	By Deformation Figures	By Critical Recrystallization	
9	3-19 hr.		
10.5	1-1.5 hr.		0.3
12.2	60-130 min.	45 min.	0.2
15	30-60 min.	9-15 min.	0.1
20.5	2-7 min.	2 min.	

As was to be expected, the fine-grained material recrystallizes faster than the large-grained, for both common lead and acid lead. This difference is particularly marked with acid lead, in the lower deformation region.

Small amounts of impurities markedly increase the time of recrystallization. Of those investigated, silver is undoubtedly the most effective. The addition of 0.0084 per cent Ag to high-purity lead increases the time of recrystallization several thousand fold. This is in qualitative agreement with the results of Russell, but differs as far as quantitative comparisons can be made. Russell finds that electrolytic lead with the

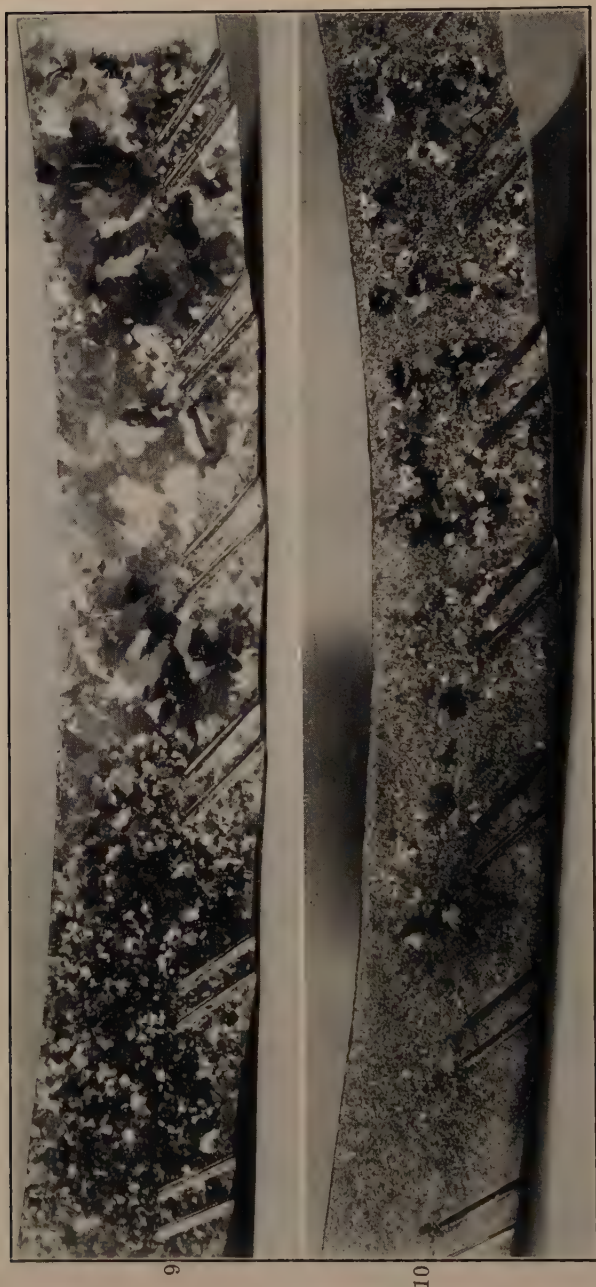


FIG. 9.—STRIP OF HIGH-PURITY LEAD INDENTED AT VARIOUS INTERVALS AFTER ROLLING; ANNEALED, ETCHED.

FIG. 10.—STRIP OF SILVER-LEAD ALLOY INDENTED AT VARIOUS INTERVALS AFTER ROLLING; ANNEALED, ETCHED.

addition of 0.005 per cent Ag, cold-rolled 10 per cent, recrystallizes at 125°C . in $2\frac{1}{2}$ hr., whereas the critical recrystallization method gives approximately the same time of recrystallization at 25°C . for the same

cold-rolling on lead containing 0.0084 per cent Ag. If we assume that the time of recrystallization increases about twice for a temperature decrease of $10^{\circ}\text{C}.$, the discrepancy between the two values will be in the order of three decimal places, even without considering the difference in the silver content. For 25 per cent deformation of the same alloy, Russell obtains a time of recrystallization at $125^{\circ}\text{C}.$ of 10 to 30 min., whereas the extrapolation of the curve of Fig. 8 gives about 1 min., or less, at $25^{\circ}\text{C}.$ This means an even greater discrepancy than the previous one.

The results for high-purity lead agree much better. Russell's results for electrolytic lead at 11° to $13^{\circ}\text{C}.$, 2.5 per cent deformation, range from 30 min. to $2\frac{1}{2}$ hr. The present work gives about 8 min. for high-purity lead, 2.5 per cent deformation, at $25^{\circ}\text{C}.$ This difference of less than two decimal places might well be due to the somewhat higher temperature and higher purity of the lead used in the present work.

Fig. 8 shows that common lead and acid lead recrystallize equally fast if the deformation is about 15 per cent, or higher. Below that range, however, acid lead recrystallizes comparatively much more slowly.

CONCLUSION

The time of recrystallization at room temperature of rolled high-purity lead, common lead, acid lead, and a silver-lead alloy was determined as a function of the deformation. For common lead and acid lead, data were obtained for both coarse-grained and fine-grained material. The time of recrystallization was measured by the critical recrystallization method and by the method of deformation figures. The critical recrystallization method was shown to be in good agreement with Brinell hardness measurements when both methods could be used.

ACKNOWLEDGMENTS

The author wishes to express his thanks to the American Smelting and Refining Co. for permission to publish this paper, and to Dr. A. J. Phillips and Mr. A. A. Smith, Jr. for their interest and helpful suggestions in preparing it.

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DISCUSSION

(*W. L. Fink presiding*)

E. E. SCHUMACHER,* New York, N. Y.—The information on recrystallization times of the order of a minute or less, so readily determined by Dr. Beck's method, may make possible the explanation of certain anomalous effects that are sometimes noted when lead alloys are cold-rolled in successive stages. Obviously, a sample that received a second rolling operation before it recrystallized might be expected to have quite different ultimate properties than one that had self-annealed before the second rolling operation was performed on it.

Since our main interest with regard to leads and lead alloys is concerned with cable sheath, most of our studies at the Bell Telephone Laboratories have been made on extruded material. We have also applied Dr. Beck's procedure to extruded, aged, and then rolled samples of pure lead, grade II chemical lead, lead with 0.06 per cent Te, lead with 1 per cent Sb and lead with 0.03 per cent Ca. As has been previously reported, lead-tellurium recrystallized much more slowly than pure lead. After 40 per cent reduction by cold-rolling, pure lead recrystallized in less than 5 sec. while lead-tellurium required about 6 hr. Even more striking, lead with 0.03 per cent Ca has not recrystallized after this degree of deformation in 25 days.

Some caution must, of course, be exercised in the application of Dr. Beck's procedure to the determination of recrystallization rates in alloys. The influence of such factors as precipitation and agglomeration must be carefully considered, since obviously they must exert profound effect on grain growth, not only directly but also indirectly. For example, degree of precipitation and distributional form of the precipitated phase in an age-hardenable alloy are themselves affected by deformation.

It is interesting that in one respect Dr. Beck's results are at variance with those reported by Brinley-Jones.⁶ The latter states that lead of medium refinement is found to be immune from grain growth and to be affected only by strains severe enough to cause recrystallization. If this were true, the Beck procedure would be inapplicable to samples possessing a uniform medium grain size on recrystallization. Obviously all ranges of grain size were developed when the samples used in Dr. Beck's study were allowed to recrystallize and all of these show the critical grain growth when treated in the prescribed manner. We ourselves observed the critical grain growth even in extruded samples having equiaxed grains over a large range of sizes.

P. A. BECK (author's reply).—The several instances of applying the critical recrystallization method in Mr. Schumacher's laboratory are a source of much encouragement, particularly since his results seem to be in very good agreement with ours. In continuing this work, we have found the method useful also with acid lead, antimonial lead, various calcium-magnesium-tin-lead alloys, etc. Many of the alloys tested were of the age-hardening type, and some work has been done to detect the effect of heat-treatment on the time for complete recrystallization. The results indicated that this effect may be exceedingly large. Thus, for instance, a rolled calcium-magnesium-tin-lead alloy strip recrystallized within one day at 150°C. when the bar was quenched from 300°C. previous to rolling, but when the quenched bar was heat-treated to effect nearly maximum age-hardening before it was rolled, it did not recrystallize for several months at 150°C. When the material was overaged by annealing before rolling, the time of recrystallization was less than 6 hr. at 150°C. Apparently it is the state of dispersion of the precipitate before rolling that influences

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⁶ *Jnl. Inst. Metals* (1937).

the time of recrystallization. Further work is being done on this problem. The critical recrystallization method was consistently in agreement with the results obtained by ordinary microscopic technique, whenever both were used.

The apparent discrepancy between Brinley-Jones' results and those of the present work can be explained as follows. Interpreted in the light of the present work, Brinley-Jones showed that for a certain brand of refined lead with large initial grain size, the time of recrystallization at room temperature was very long, provided the deformation was small. Consequently, the very coarse recrystallized structures corresponding to such small deformations were practically never observed. With increasing deformation the time of recrystallization became shorter, but the resulting recrystallized structure was much finer. Therefore, in this material no amount of deformation produced coarse grains at room temperature. With smaller initial grain size, the time of recrystallization became shorter and the coarse grains, due to critical recrystallization at room temperature, developed within the period of the experiment.

The present results indicate that other conditions tending to speed up recrystallization, such as high purity and higher temperature, have an effect similar to that of smaller initial grain size. Thus high-purity lead, in spite of very large initial grain size, showed critical recrystallization at room temperature. Acid lead, or antimonial lead that did not critically recrystallize at room temperature within practicable periods of time, no matter what the initial grain size, readily showed critical recrystallization at elevated temperatures. Super-refined lead with an impurity content roughly corresponding to that of Brinley-Jones' material occupies an intermediate position. Fine-grained samples stored for several days at room temperature often showed critical recrystallization if their previous handling involved a certain small amount of straining, whereas large-grained samples were immune from critical recrystallization under the same conditions. However, critical recrystallization was always achieved (after initial straining) at the elevated temperatures used in the present work.

Finally, I want to stress the importance of Mr. Schumacher's statement regarding the rolling of lead in successive stages. Three different alternatives could be clearly distinguished in this process: (1) the material completely recrystallized between successive passes in the rolls; (2) partial recrystallization took place between passes; (3) practically no recrystallization took place between passes. The first case occurred when common lead or acid lead were rolled in 30 per cent passes to produce fine-grained material. The second alternative was found to occur when these same brands of lead were rolled in 10 per cent passes in order to produce large-grained material. The third alternative occurred when rolling calcium-magnesium-tin-lead alloys and antimonial leads. It is clear that in the second case the period of time between individual passes is an important factor, in so far as it influences the amount of deformation remaining in the material at the time of the next pass.

A Simple Method of Thermal Analysis Permitting Quantitative Measurements of Specific and Latent Heats

BY CYRIL STANLEY SMITH,* MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

THE method of thermal analysis, so important in the development of metallographic science, has of recent years been falling into disuse owing to the development of other physical methods which give results easier of interpretation and which can be used for the study of either equilibrium or transitional conditions because they do not require a continuously changing temperature. Nevertheless thermal analysis remains useful in the study of reactions that take place rapidly, and the simplicity of the experimental technique and the general availability of the apparatus involved are points in its favor.

Theoretically, thermal analysis is capable of giving specific and latent heat measurements and therefore should permit the study of reactions on a more fundamental basis than any other method. It is, however, difficult or impossible to obtain quantitative heat measurements from cooling curves obtained in the usual way. Even if the furnace containing the sample is cooled or heated at a linear rate, or if a gradient furnace is employed to maintain a constant rate over a large range of temperature, the heat flow from or to the specimen depends on its previous history, for the difference of temperature between the specimen and its surroundings varies. The emissivity of the specimen surface, moreover, is unlikely to be constant. The able mathematical analysis by Russell,¹ although it prevents misinterpretation of data, has an effect rather the reverse of that intended, and leaves the reader doubtful of the possibility of ever obtaining quantitative results from thermal curves.

Nothing can be done to apply thermal analysis to the study of equilibrium conditions of reactions that are not completed at rates of temperature change above about 1° C. per minute, and this unfortunately excludes most solid transformations in alloys.† For the determination of liquidus

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¹ References are at the end of the paper.

† Thermal analysis can be sometimes used to determine the presence or absence of a phase after long annealing to obtain equilibrium, for if the sample is then cooled or heated at a convenient rate an arrest will appear if the phase is present at some temperature characteristic of the rate of cooling, even though it is far removed from the equilibrium temperature.

temperatures and peritectic or eutectic horizontals, the ordinary cooling curve is often sufficient, because all that is necessary is the temperature of inflection, and quantitative heat measurements are meaningless because of segregation and the lack of approach to equilibrium. In the rather limited field where reactions are fast enough and where quantitative heat measurements are desired, the following method will be found useful. It is suitable for the determination of heats of reactions that occur with reasonable rapidity, and rates of transformation, precipitation, or ordering on progressive heating or cooling. The method also seems to have utility in the determination of specific heats with fair accuracy and great ease, employing only apparatus available in every metallurgical or physical laboratory.

PRINCIPLE OF METHOD

Briefly, the new method consists in placing the specimen with its thermocouple in a refractory container of low thermal conductivity and placing this in a furnace the temperature of which is maintained a constant amount above or below the specimen temperature. This is easily managed by opposing the electromotive force of the specimen couple to that of a couple at the outside of the container, and feeding the resultant electromotive force to an automatic temperature controller of ordinary design. Alternatively a differential couple may be used, independent of the specimen couple, with one junction inside and another outside the container.* In this way a constant temperature gradient is maintained across the container walls and, since the thermal conductivity of the refractory remains constant at a given temperature, the heat flow through it will be constant, and so the heat received or lost by the specimen in a given elapsed time will be constant. Obviously, therefore, the time taken for the specimen to move through a given temperature interval will be proportional to the heat absorbed or evolved.

Actually, the conductivity of any refractory does not remain exactly constant as the temperature changes, neither does the electromotive force difference of opposed thermocouples remain independent of tem-

* The differential couple is to be preferred for accurate determinations of specific heat. The two-couple method is perhaps simpler to construct and use but it necessitates a controller of high resistance (at least 300 ohms). The ordinary potentiometer controller is of low resistance and will affect the main thermocouple readings appreciably when it is slightly out of balance during the control cycle. It is, of course, important that the controller have a short cycle and that the furnace have as little lag as possible. Control of the average temperature within 0.5°C. is desirable but a reproducible cycle larger than this is harmless if of short duration. If the controller is compensated for cold-junction temperature changes (as are most commercial instruments) it is necessary to eliminate this or to place a thermocouple with one junction in ice and the other at instrument temperature, connected in series with the electromotive force to be controlled.

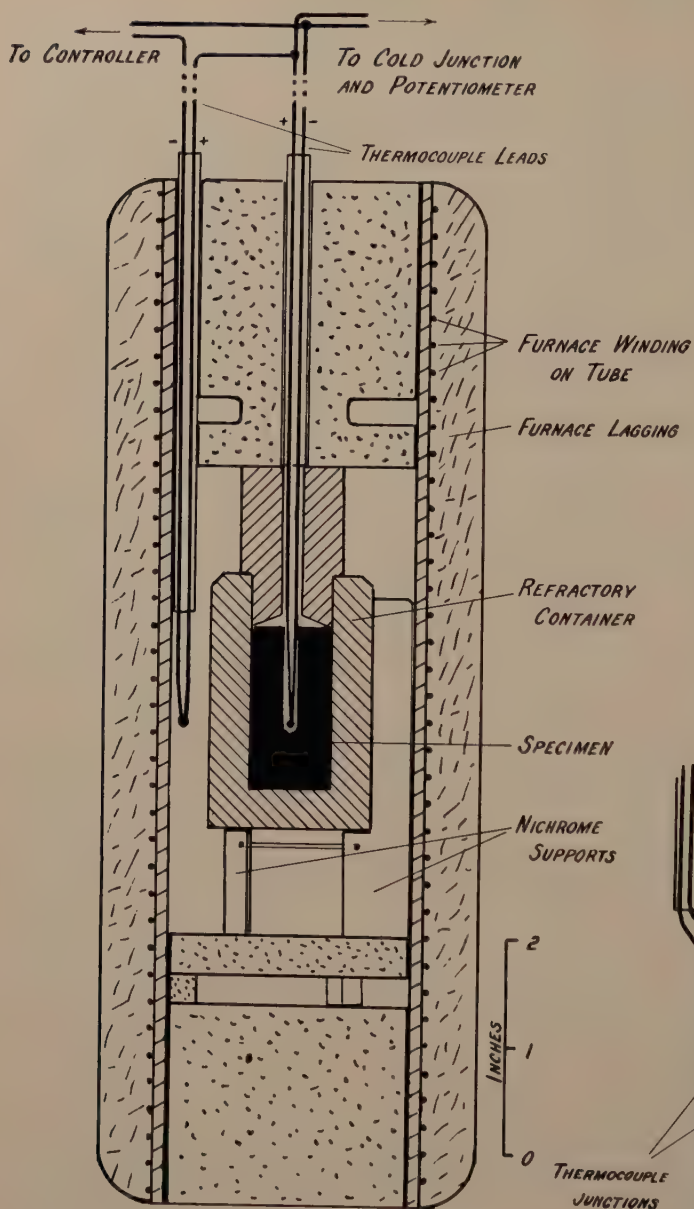


FIG. 1.

FIG. 1.—APPARATUS FOR THERMAL ANALYSIS.

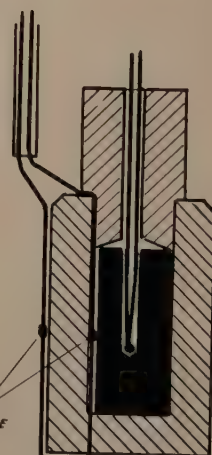


FIG. 2.

FIG. 2.—ARRANGEMENT OF DIFFERENTIAL COUPLE FOR CONTROLLING TEMPERATURE GRADIENT ACROSS CONTAINER.

perature, consequently the heat flow varies slightly with temperature. However, a given container can be calibrated over a range of temperatures by use of a mass of known specific heat and will give reproducible quantitative results.

Fig. 1 shows a setup which has proved satisfactory. The specimen (0.75-in. diameter, 1.5 in. long) fits closely in a container with walls 0.375 in. thick, turned on a lathe from a piece of Armstrong "Non Pareil" insulating brick. This material is said to have a thermal conductivity of 0.00028 c.g.s. units at 150° C. and 0.00044 at 870° C., the maximum temperature at which it should be used. When a temperature difference of 60° was maintained, the heat flow through this container varied between 0.92 cal. per second at 200° C. and 1.23 at 600°. For higher temperatures a crucible of Armstrong LW20 insulating brick (conductivity = 0.0006 to 0.0008 c.g.s. units at 540° to 1315° C.) was used. Both these materials were found satisfactory but obviously any insulating material of suitable refractoriness, mechanical characteristics and constancy could be used. The container was given a wash of alundum cement to fill surface pores. It was found necessary to dry it by heating immediately before use, as it was distinctly hygroscopic. The furnace consisted of a thin alundum core, 2½ in. in diameter, uniformly wound with Nichrome wire. To obtain a cooling rate sufficiently rapid for thermal analysis very little lagging (½ in.) is necessary but a furnace for heating curves alone may be well insulated. The container is supported on Nichrome spacers to allow free circulation of air around and below it.

SPECIFIC HEAT MEASUREMENTS

If it is desired to make quantitative heat measurements it is necessary first to calibrate the container by determining its rate of heating when empty and then with a sample of known specific heat. Copper is a suitable standard, since it undergoes no transformation and its specific heat is known fairly accurately over a wide range of temperature.²

The rate of heat flow through the container is equal to the product of its conductivity and a constant depending on its size and shape, multiplied by the temperature difference between its inner and outer surfaces. With a given container the first two factors are constant and the temperature difference is maintained constant experimentally. The resulting constant heat flow serves to supply the specific heat of the sample, its heat of transformation, if any, and the specific heat of an indeterminate part of the container itself; i.e.,

$$H \times \Delta t_1 = \Delta T_1 \times C_1 W_1 + L_1 W_1 + \Delta T_1 \times C_r W_r \quad [1]$$

where H is the heat flow per unit time; C_r , C_1 and W_r , W_1 are the specific heats and masses of the effective part of the container and of the speci-

men, respectively; ΔT is the change of temperature in time Δt ; and L_1 is the latent heat of any transformation that may occur in the temperature range of ΔT .

If a second sample of heat capacity C_2W_2 is substituted, then (if no transformation occurs in either sample so that latent heat may be omitted), by the use of the equation for the empty container ($H \times \Delta t_r = \Delta T_r \times C_rW_r$)

$$\frac{C_2W_2}{C_1W_1} = \frac{\frac{\Delta t_2}{\Delta T_2} - \frac{\Delta t_r}{\Delta T_r}}{\frac{\Delta t_1}{\Delta T_1} - \frac{\Delta t_r}{\Delta T_r}} \quad [2]$$

The figure $\frac{\Delta t}{\Delta T}$ is the slope of a time-temperature curve, or the figure obtained directly for an inverse rate curve* in the usual way. In the equations above, the subscripts r , 1 and 2 denote respectively this figure for the empty container and for the container with specimens 1 and 2. The heat capacities of samples are thus directly proportional to the values of $\frac{\Delta t}{\Delta T}$ after they have been corrected by subtracting a blank reading obtained from a heating or cooling curve of the container alone. Because of the shape of the container and the nonuniform temperature gradient in it, the correction will be greater on cooling than on heating. When latent heats are involved it is necessary to determine H at the appropriate temperature, by substituting the experimental times from a blank and standard run; i.e.,

$$H = \frac{C_1W_1}{\frac{\Delta t_1}{\Delta T_1} - \frac{\Delta t_r}{\Delta T_r}}$$

The latent heat of a transformation causing an arrest at constant temperature is directly proportional to the duration of it ($LW = H\Delta t$ when

* Most conveniently this is the time for a temperature change equivalent to an electromotive force change of 0.05 mv. with a chromel-alumel thermocouple rather than a specific temperature interval. In making the time measurements for an inverse rate curve, whether these are to be used for specific heat measurements or ordinary thermal analysis, it is desirable to have the galvanometer zero mark directly on the face of the clock. The clock (preferably reading in hundredths of a minute instead of seconds) is placed alongside the potentiometer at a convenient angle for reading, and the light beam reflected down to it by a mirror. This makes it unnecessary to change the focus of the eye when passing from the galvanometer index to the clock, and readings good to ± 0.01 min. are readily obtained over prolonged periods with little eye fatigue. Entirely automatic devices for plotting inverse rate curves have been constructed. A good commercial recording potentiometer will give a time-temperature curve, the slope of which can be measured with sufficient accuracy for many purposes.

$\Delta T = 0$). If a transformation occurs over a range of temperature, its latent heat will appear as apparent specific heat.

It is obvious that a highly polished surface on the sample would result in an appreciable temperature difference between it and the inner walls of the container. For this reason it is desirable to roughen the surface of the specimen and to coat it with a material of high emissivity unless it is to be in actual thermal contact with the container.* If the junction

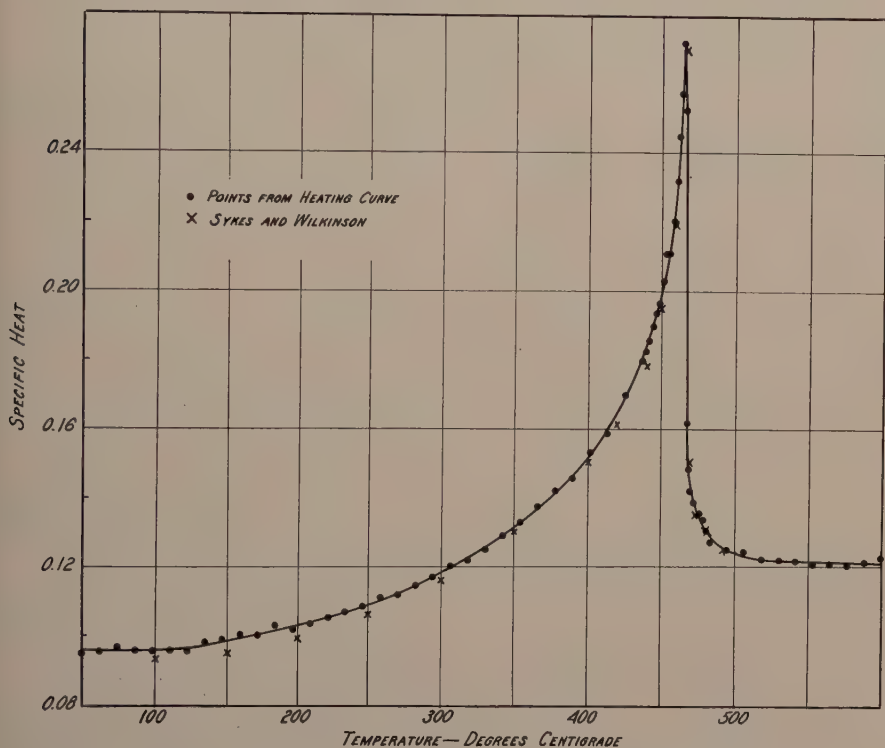


FIG. 3.—SPECIFIC HEAT OF BETA BRASS AS OBTAINED FROM A HEATING CURVE.

of the inner controlling couple is against the wall of the container, the sample will lag but nevertheless will receive the standard heat flow, except after an arrest. For this reason the differential couple is to be preferred in specific heat measurements. Another disturbing factor lies in the fact that the temperature gradient within the container walls is not linear, since the temperature is changing, and the container correction therefore varies with heating rate. These and other effects, however,

* A saturated solution of copper nitrate dried on the surface of the specimen and heated to 300° C. provides a good black on copper alloys except in reducing atmospheres. Commercial heat-radiating paints are available and probably would be satisfactory.

are small and are largely eliminated if the standard sample has a size, heat capacity and emissivity of the same order of magnitude as the other samples to be tested.

Fig. 3 shows the specific heat of beta brass obtained from a heating curve. The sample weighed 86.6 grams and contained 48.10 per cent zinc by weight. With the container described above and a temperature difference of 60° C. (controlled with a differential couple) the assembly

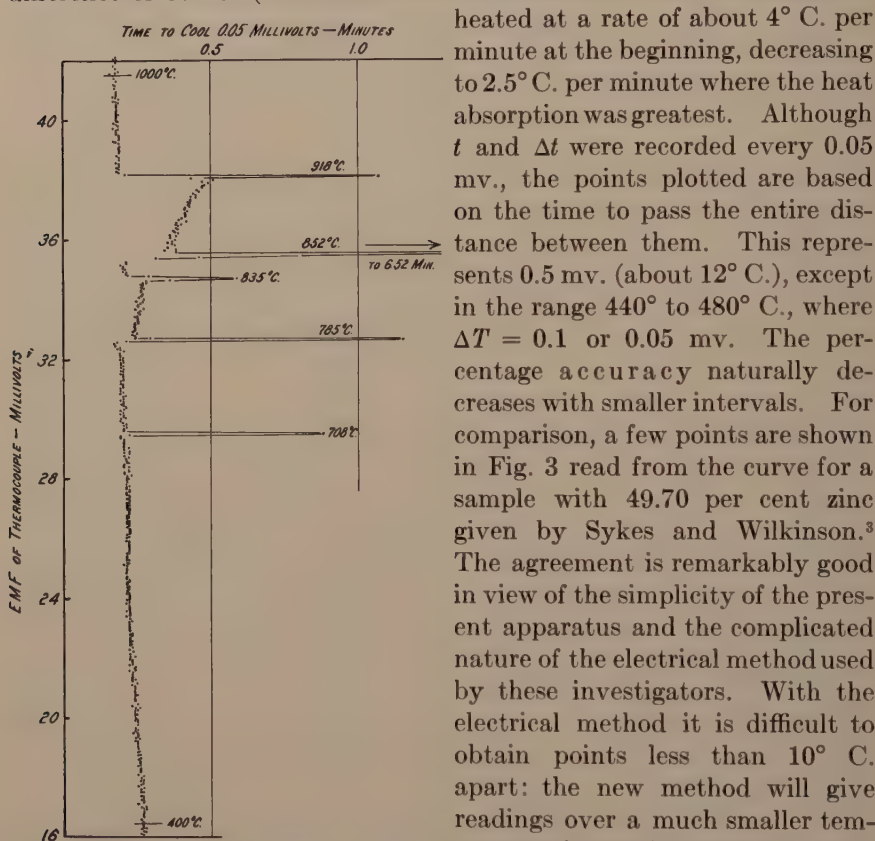


FIG. 4.—COOLING CURVE OF COPPER-SILICON ALLOY CONTAINING 6.3 PER CENT SILICON.

Note absence of accelerated cooling following arrests and constancy of cooling rate at all temperatures.

measurements when cooling just as well as on heating.

COOLING CURVES

Even if quantitative heat measurements are not needed, as in the ordinary thermal analysis of alloys to obtain transformation temperatures, the method of control is useful in that the heat flow from the

specimen is maintained constant and there is not a rapid removal of heat after an arrest. The furnace temperature is held constant throughout an arrest and does not commence to fall until the specimen itself cools. As a result, temperature gradients within the specimen and along the thermocouple are smaller and arrests are sharper. Interpretation of the curves is very easy, for they directly reflect the changes taking place in the specimen. The decrease in cooling rate at lower temperatures that is characteristic of ordinary curves is completely avoided. If no arrests occur, the rate of cooling over the whole temperature range varies only to the extent that the thermal conductivity of the refractory and the specific heat of the sample change. The rate of cooling or heating can be changed at any time by merely changing the setting of the temperature-difference controller. The new method obviates the necessity for gradient furnaces or linear control devices and is much simpler than any of them.

Fig. 4 is an example of the type of cooling curve obtainable. This is of a 150-gram sample of a copper-silicon alloy containing about 6.3 per cent silicon. It was placed in a container like that of Fig. 1, but $1\frac{1}{4}$ in. in internal diameter and made of LW20 refractory. The various arrests are caused respectively by the liquidus, peritectic formation of beta, kappa formation, beta decomposition and gamma formation. Note the sharpness of the arrests and the virtual absence of accelerated cooling at their termination. The decrease in latent heat resulting from the decreased amount of alpha solidifying in a given temperature range, as the horizontal spread between solidus and liquidus increases, is clearly shown. The specific heats of the alloy in the liquid, alpha + beta, alpha + gamma, and alpha + delta fields are approximately the same, while in the kappa + beta region the progressive rapid formation of kappa from beta contributes latent heat and so increases the apparent specific heat of the sample in this range.

SUMMARY

The specimen is placed in an insulating refractory container across which a constant temperature gradient is automatically maintained. Heat flow to the sample depends only on the constants of the container, which may be determined by the use of a sample of known specific heat. The time taken to cool or heat through a given temperature interval (after a blank correction) is directly proportional to the heat capacity of the sample, and the duration of an arrest is directly proportional to the latent heat. The method of control eliminates accelerated cooling following prolonged arrests and provides a simple way of obtaining a constant cooling rate at all temperatures, thus replacing elaborate gradient furnaces. Examples are given, including a determination of the specific heat of beta brass.

REFERENCES

1. T. F. Russell: The Interpretation of Thermal Curves and Some Applications to Ferrous Alloys. Iron and Steel Inst. Advance Copy No. 10 (May 1939).
2. Metals Handbook, 1939 Edition, 1382.
3. C. Sykes and H. Wilkinson: The Transformation in the Beta Brasses. *Jnl. Inst. Metals* (1937) **61**, 223-239.

DISCUSSION

(A. Allan Bates presiding)

J. B. AUSTIN,* Kearny, N. J.—What is the effect of thermal conductivity of the sample on the accuracy of measurement? Specifically, in the author's opinion is the method applicable to powders, cuttings, or refractory materials whose thermal conductivity is small compared to that of a metal, especially if calibrated on a material of approximately the same thermal conductivity?

No details are given for calculating the latent heat cases where it is spread over a range of temperature and appears as apparent specific heat. I assume that it can be done by integrating the area under the anomalous part of the heat curve.

G. EDMUNDS,† Palmerton, Pa.—We constructed an equipment based upon the principles described by Dr. Smith, but with a few alterations. Our equipment contains, instead of the refractory container shown in Dr. Smith's Fig. 1, two concentric Nichrome cylinders, inside of which is placed a thin-walled crucible, either of graphite or other suitable material. To the Nichrome cylinders are welded several Alumel wires, thus providing multijunction thermocouples that operate a controller for the furnace windings and thus maintain the temperature difference between the Nichrome cylinders. An additional thermocouple is used for measurement of the melt temperature.

One of the major advantages of Dr. Smith's method is that it makes possible the detection of any small heat effect at a temperature only a few degrees below that at which a major effect has occurred.

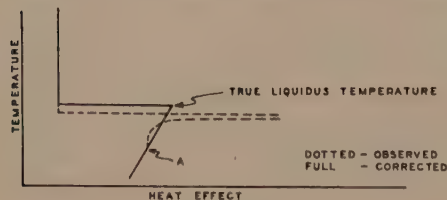


FIG. 5.

With the conventional differential thermal-analysis method sufficient stabilization after a large heat effect for the detection of a small one may not occur until the specimen has reached a temperature of as much as 30° to 50°C. from that at which the large effect occurred. Fig. 4 shows only slight irregularities following major heat effects.

While our construction has not been compared directly with that used by Dr. Smith, calculations indicate the heat capacity of the thin Nichrome cylinders to be less than equivalent refractory insulation. This leads to a closer control of the temperature differential and reduces further the time required for stabilization of conditions following a major heat effect from the specimen.

The cooling curves obtained by any method, whether using the new method of control or not, generally show a very large thermal effect at the beginning of freezing. Apparently this is due to undercooling of the melt, resulting in the evolution of much

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† Investigator, Research Division, The New Jersey Zinc Co.

heat when crystallization begins. In a curve such as Fig. 4 the time of cooling 0.05 mv. at 918°C. amounted to about 1.1 min. whereas cooling with crystallization at the normal rate required but 0.5 min. just afterward. Had crystallization started as soon as the liquidus was reached, the heat effect would have been so distributed as to continue curve *A* in Fig. 5 upward about two of the 0.05-mv. divisions, and the curve in this neighborhood would then be as shown in Fig. 5. This type of correction has been made to all of our curves and often has been found to be of major importance, since supercooling of many degrees frequently occurs.

C. S. SMITH (author's reply).—Because of the large temperature gradients that otherwise will occur, I do not believe the method can generally be applied to specimens that have a conductivity less than about 10 times that of the refractory container.

Dr. Austin himself answers his second question. If the specific heat is known or can be estimated, it can be subtracted from the total heat measured in the temperature range concerned and the latent heat obtained. By determining the apparent latent heat at successive temperature intervals during the not-too-fast cooling of a piece of steel, for example, the rates of transformation at these temperatures can be obtained immediately.

Mr. Edmunds' design of apparatus using a Nichrome shield instead of solid insulation renders the apparatus stronger and is to be preferred for the detection of thermal critical points. It seems likely, however, that solid refractory insulation would be more reproducible and constant than the other type, and would change to a smaller extent with temperature. The correction of liquidus temperatures suggested by Mr. Edmunds is fundamentally sound. It should also be applied to any thermal curves but is not precise except when the rate of heat flow is constant. It is easier to make this correction graphically on a time-temperature curve than upon an inverse-rate curve: The true liquidus temperature is just the point of intersection of the curve for the liquid state with the extrapolation of the part of the time-temperature curve that corresponds to the liquid + solid state after the first arrest due to supercooling.

Many years ago White⁴ used two thermocouples in a furnace for thermal analysis and attempted quantitative interpretation on the basis of temperature differences. The present scheme is novel in the use of automatic control of the temperature difference and the use of insulation. This results in a constant reproducible heat flow instead of the variable conditions existing when a naked crucible is placed in an indefinitely cooling furnace.

⁴ W. P. White: Melting-point Methods at High Temperatures. *Amer. Jnl. Sci.* (1909) [iv]28, 474-489.

A Metallographic Study of Internal Oxidation in the Alpha Solid Solutions of Copper

BY FREDERICK N. RHINES,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

PURE copper that has been allowed to oxidize at an elevated temperature in the air is found to be covered with two distinguishable layers of oxide scale. The outer of these, which is very thin, is composed of cupric oxide, while the inner layer, comprising the bulk of the scale, is made up chiefly of cuprous oxide (Fig. 1a). If a small quantity of an alloying element, such as silicon, is present in the copper, silica particles are found disseminated through the cuprous oxide, deposited most abundantly near the metal surface, and, in addition, silica particles occur to a limited depth within the copper itself (Fig. 1b). It is this inner layer, composed of oxide particles precipitated in a matrix of metallic copper, that is known as the "subscale" or the zone of internal oxidation. Under a low oxygen pressure it is possible to produce the subscale without the formation of external layers of copper oxides, thus leaving the metal surface bright and apparently clean while oxidation has occurred, in fact, to a considerable depth within the metal (Fig. 2).

Although little is yet known in a detailed way of the mechanism of internal oxidation, the general nature of the process is evident. By virtue of the considerable solubility of oxygen in copper,¹ it is possible to bring the alloying element in contact with oxygen within the metallic solid solution. If the oxide of the alloying element is more stable than cuprous oxide, the foreign oxide may form and, since most oxides are relatively insoluble in copper, it will not long remain in solution, but will separate as a precipitate. As the metallic solute is exhausted in the zone of precipitation, oxygen that is constantly being supplied at the surface diffuses farther into the alloy and thus produces an ever-thickening shell of subscale. The distribution of the reacting elements in the subscale and adjoining zones must be somewhat as indicated in Fig. 3.

The conditions requisite to internal oxidation to be anticipated are thus: (1) a solubility of oxygen in the alloy, (2) the ability of oxygen to diffuse at an appreciable rate into the alloy, (3) the possibility of the

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* Member of the Staff of the Metals Research Laboratory and Assistant Professor of Metallurgy, Carnegie Institute of Technology, Pittsburgh, Pa.

¹ References are at the end of the paper.

formation by the alloying element of an oxide more stable than the oxide of the host metal and (4) a relatively low solubility of this oxide in the metal. To these may be added the equally evident condition that the constitution of the system, regarded as a ternary alloy composed of the solvent metal, the solute metal and oxygen, must be such

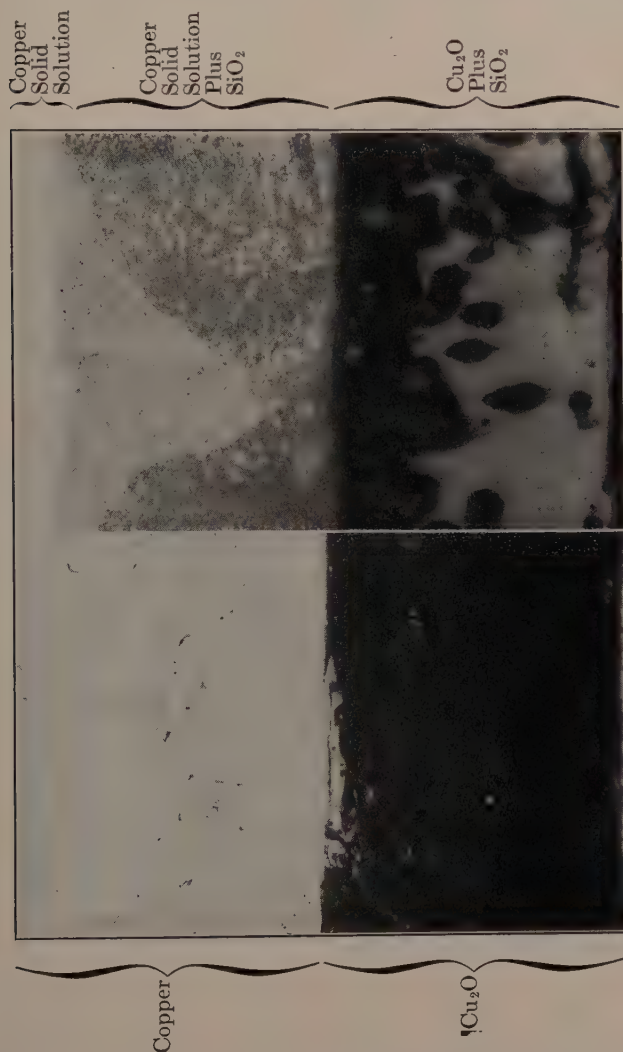


Fig. 1.—SCALE ON COPPER AND COPPER ALLOY.
a. Copper oxide scale on pure copper, $\times 150$, heated 2 hours at 1000°C . in air. Dark area is all cuprous oxide, cupric oxide layer being too thin to be revealed by polishing technique used.
b. External and internal scale on copper-silicon alloy, $\times 150$, heated 2 hours at 1000°C . in air.

that a quasibinary equilibrium may occur between the solid solvent and the precipitating oxide at the temperature of oxidation.

An ideal diagram illustrating the constitution of such a system is shown in Fig. 4. For the sake of simplicity, only one oxide is indicated for each metal. If the oxidation is carried out at a fixed temperature an

isothermal section is adequate to describe the relationships. Representing by Z the composition of the binary alloy that is to be subjected to oxidation, there would form upon Z a series of layers whose compositions would occur along the dotted line connecting Z with the oxygen corner of the diagram. Strictly speaking this will happen only in the improbable event that there is nowhere in the layers formed any change in the relative proportions of A and B , but, for the moment, let it be assumed that such is the case.

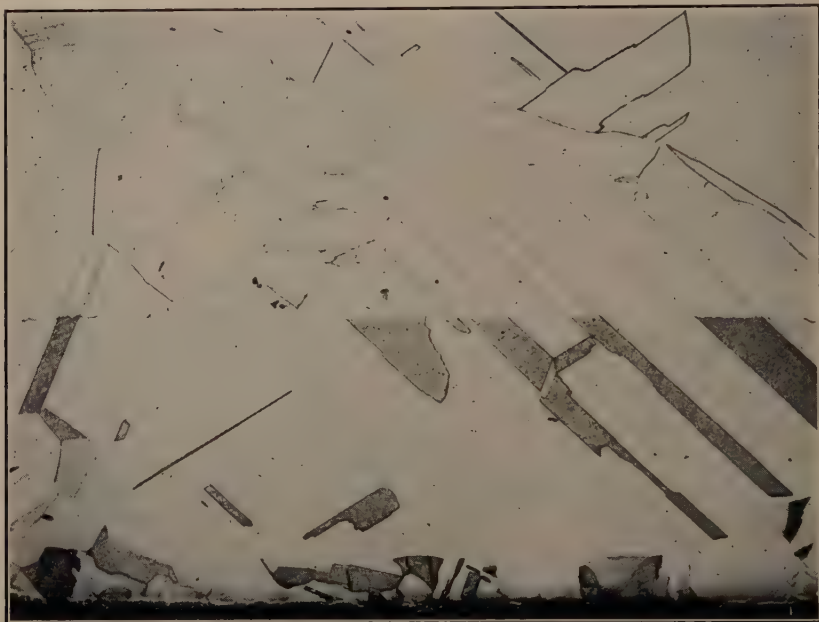


FIG. 2.—INTERNAL OXIDATION IN ALLOY OF COPPER WITH 0.103 PER CENT SILICON.
× 50.

Sample oxidized at low oxygen pressure has no external scale. Internal oxidation is marked by gray zone crossing lower half of picture.

The succession of zones through which the dotted line passes is seen to be: β solid solution, $\beta + \text{AO}$, $\beta + \text{BO} + \text{AO}$, $\text{BO} + \text{AO}$, $\text{BO} + \text{AO} + \text{O}$, $\text{BO} + \text{O}$, and oxygen gas. In the photomicrograph of Fig. 1b, it is evident that only the one-phase and two-phase zones correspond to scale layers on the sample. The reason for this is clear: the layers form by the inward diffusion of oxygen; this diffusion may take place only in the presence of a gradient; no gradient of oxygen may exist at equilibrium in a three-phase ternary system, for in such a case the concentrations of all components are fixed; therefore, the three-phase zones in the diagram must correspond to interfaces rather than to layers. Stated in another way, only the regions in the ternary isothermal section that retain one or more degrees of freedom correspond to layers in a ternary composite formed by isothermal diffusion.

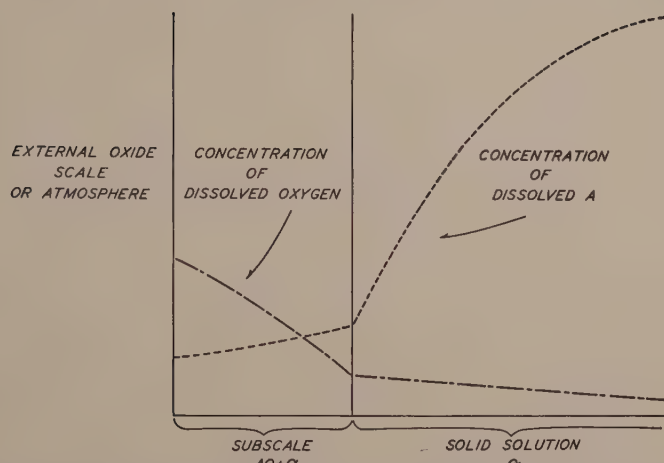


FIG. 3.—SCHEMATIC REPRESENTATION OF DISTRIBUTION OF DISSOLVED OXYGEN AND ALLOYING ELEMENT A IN SUBSCALE AND UNOXIDIZED SOLID SOLUTION.

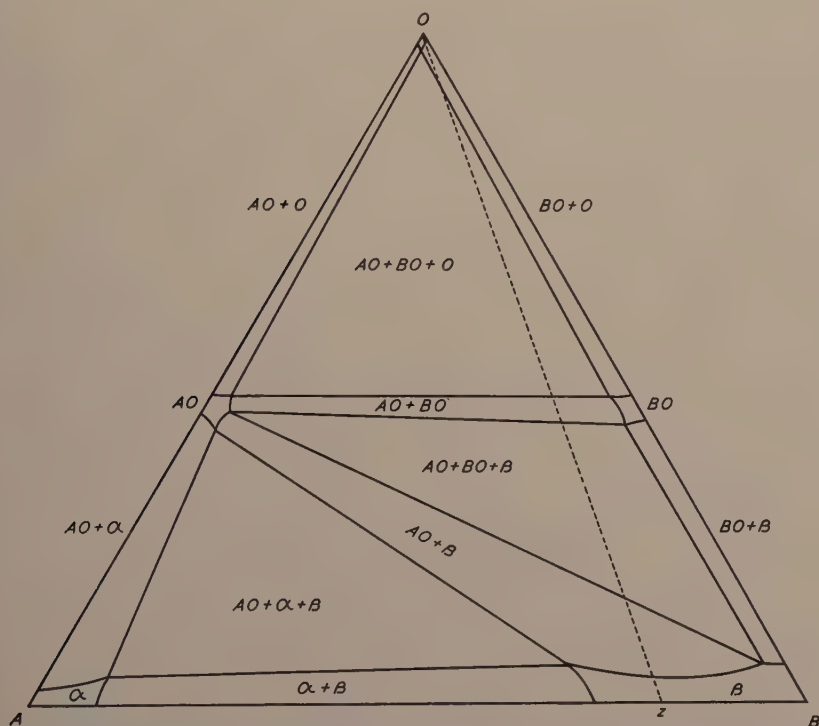


FIG. 4.—SCHEMATIC REPRESENTATION OF ISOTHERMAL CONSTITUTION OF TERNARY ALLOY SYSTEM COMPOSED OF TWO METALS AND OXYGEN WHERE EACH METAL FORMS BUT ONE OXIDE.

The same argument may be applied to higher order systems whereby it is found that in the oxidation of ternary alloys the maximum number of phases in any one layer will be three, in quaternary alloys four, and so on.

Returning to the possibility of local variations in the relative proportions of the A and B components of the alloy, it is clear that such a condition would result in a localized lateral shift in the dotted line of Fig. 4. Physically this condition could be brought about by the inward or outward diffusion of one of these elements, the magnitude of the shift in each zone being dependent upon the relative rates of diffusion of oxygen and the metals in the corresponding layer. If the shift is slight the structure of the scale would differ from the "ideal" only in the distribution of the phases within each individual layer from that arrangement demanded by the tie lines. Large deviations, of course, would altogether vitiate the predictions of the diagram. Fortunately, however, oxygen diffuses through copper* much more rapidly than do any of the metals whose diffusion behavior has been studied,† whereby it is anticipated that internal oxidation will follow the predicted course. Conditions in external oxidation are undoubtedly much less simple.

Obviously the case discussed above is but one of several types likely to be encountered. It does appear, in fact, to describe the conditions found in most of the alloys studied in the present research. Nevertheless, a brief consideration of some of the other possibilities may prove interesting.

Binary alloys of the α phase (Fig. 5) may be expected to behave in either of two ways. If of composition t they might form a layer of mixed metal and oxide of the base metal between the purely metallic and wholly oxidized layers. The oxygen gradient within either phase of the field $A_2O + \alpha$ would almost certainly be small, resulting in a thin two-phase layer, which with any appreciable intermetallic diffusion might disappear altogether. Composition y on the β side is of the same type. If the alloy is of the composition u there should form two new layers containing metallic phases. The first of these, next to the α solid solution, would be formed by the precipitation of particles of the B-rich β phase; the second, predominantly oxide of the metal A, would also contain particles of β . Copper containing small additions of silver has been found to behave approximately in this way. Composition v is similar except that

* C. E. Ransley, in a prepublication abstract,² reports the diffusivity constants of oxygen in copper as 1.1×10^{-9} sq. cm. per sec. at 600°C. and 2.1×10^{-6} sq. cm. per sec. at 950°C.

† F. N. Rhines and R. F. Mehl³ reported the diffusion coefficients of Al, Be, Si, Sn and Zn near zero concentration to be of the order of 8×10^{-12} sq. cm. per sec. at 600°C. and 3×10^{-9} sq. cm. per sec. at 950°C. Thus oxygen diffuses through copper hundreds of times as fast as do any of these metals.

in this instance the zone of $A_2O + \beta$ may be predominantly metallic. Alloys w and x are of peculiar interest because they show that with a small change in the composition the first layer of subscale may be changed from one of $\beta + A_2O$ to one of $\beta + AO$. In addition a double subscale involving each oxide separately may form upon alloy w . This type of action has been found in silver-base alloys containing various small quantities of copper where the oxides precipitated internally are CuO and Cu_2O . For the purposes of the present paper the behavior of initially polyphase alloys need not be discussed.

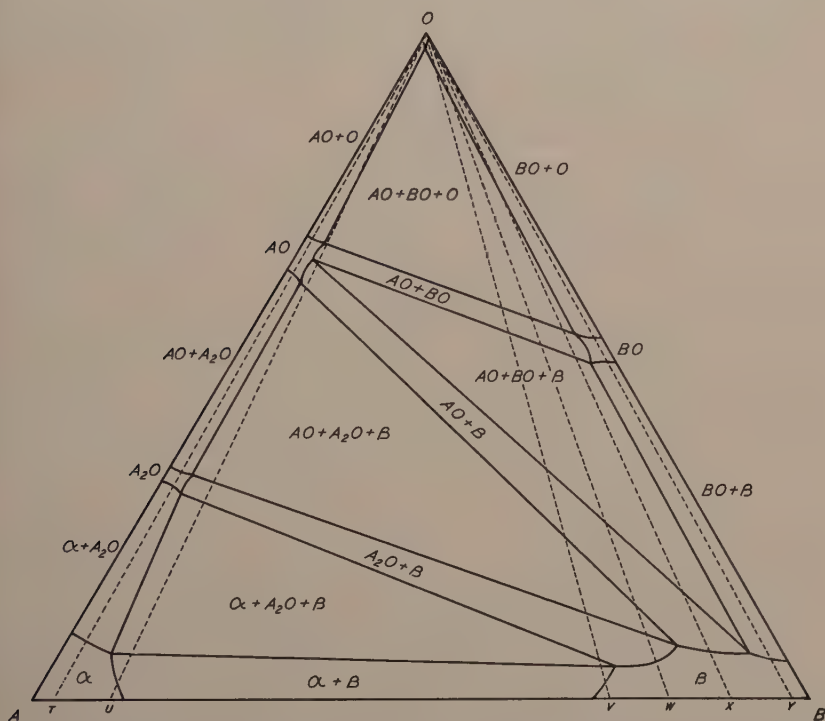


FIG. 5.—SCHEMATIC REPRESENTATION OF ISOTHERMAL CONSTITUTION OF TERNARY ALLOY SYSTEM COMPOSED OF TWO METALS AND OXYGEN WHERE ONE METAL FORMS TWO OXIDES AND OTHER BUT ONE.

These considerations may be employed to indicate in a general way the range of conditions under which internal oxidation is to be expected in industrial practice. The alloys of metals forming very stable oxides such as those based upon aluminum or magnesium should be largely, if not entirely, immune to internal oxidation because the oxides of most of the common addition agents would in this case be less stable than those of the host metal, while the alloys of the precious and semiprecious metals that involve additions of the less noble metals should all be subject to internal oxidation. To a lesser extent alloys based upon copper,

nickel, iron, zinc, lead and tin may be expected to form subscales, but only in those oxidized at high temperatures should the effect be extensive.

The conditions of annealing that will allow internal oxidation are somewhat broader than those leading to surface scaling. Even bright-annealing operations may cause the formation of subscale while the metal surface remains clean when there is some free oxygen present in the atmosphere. With some alloys, particularly at high concentrations of the alloying agent, the external oxidation proceeds at such a rate that it overtakes the internal oxidation and thus eliminates the subscale. These compositions may, therefore, be subject to internal oxidation under certain conditions of bright annealing while being apparently immune if oxidized freely in the air.

The practical importance of the existence of a subscale upon an alloy product no doubt depends to some extent upon the physical form and distribution of the oxide particles as well as upon the nature of the use to which the product is to be put. Certain working operations—for example, drawing—are extremely sensitive to surface defects in the metal and one might expect subsurface deposits of oxides to be objectionable. Although relatively little has been published upon the subject, some such effects have been recognized for a long time. In 1912 Turner⁴ wrote of the annealing of brass, “if the atmosphere is oxidizing a certain amount of oxide of zinc may also be produced in the alloy and rottenness result.” More recently both Blazey⁵ and Wyman⁶ have remarked upon the occurrence of internal oxidation in the course of studies upon the embrittlement of commercial copper during annealing. Presumably, the oxidizing element was bismuth or arsenic in the copper used by Blazey and some residual deoxidizing agent in Wyman’s copper. In neither case, however, was the role of internal oxidation judged to be as significant as that of other factors in causing embrittlement.

Not all of the practical aspects of internal oxidation are disadvantageous, however, for the ancient process of the blanching of silver-copper alloys and the more modern practice of improving the conductivity of copper by means of an oxidizing anneal that precipitates oxides of some impurities are both dependent upon internal oxidation. Perhaps, with an increased understanding of the process further uses may be found.

Exploratory investigations of internal oxidation have been carried out in a number of laboratories during the past decade. C. S. Smith,⁷ who identified and described the effect in alloys of copper with small additions of cobalt, silicon, aluminum, nickel and chromium, and who measured the rate of growth of the subscale as a function of temperature in an alloy of copper and silicon, appears to be the first to have studied the subject intensively. He is responsible too for introducing the term “subscale” in the sense in which it is being used here. More recently Froelich,⁸ in a general survey of the oxidation behavior of copper alloys,

has noted the occurrence of internal oxidation in alloys containing lithium, phosphorus, manganese, calcium, titanium, tin, and zinc, but has made no detailed study of the phenomenon in any of these systems.

Similar precipitation structures associated with the penetration of oxygen into an alloy have been observed by a number of investigators. Among them, Leroux and Raub⁹ found both cupric and cuprous oxide precipitating internally in silver-copper alloys, the cupric oxide occurring in alloys poor in copper and the cuprous oxide in those rich in copper. Others¹⁰⁻¹⁵ investigating the scaling properties of ferrous alloys, have mentioned internal oxidation in a number of special steels, notably those containing aluminum, silicon, tungsten, manganese, and phosphorus. In almost all such cases the steels have been of such a complex nature, however, that the evaluation of the results has been difficult.

The present program contemplates a general study of the nature of the process of internal oxidation followed by quantitative measurements of such elements of the process as may appear useful, among which are the rates of penetration in various systems, the effect upon mechanical properties and perhaps others. This paper is devoted to a metallographic exploration of the factors that influence internal oxidation, both with regard to their identification and to the examination of their qualitative effect upon the structure of the subscale and its rate of growth. Because of their known response to internal oxidation and the ease with which alloys of reasonably high purity can be made, the copper-base systems have been selected for this purpose.

EXPERIMENTAL PROCEDURE

The alloys used were made in the laboratory from oxygen-free high-conductivity copper and the purest grades of alloying elements available at the time. In Table 1 are listed the compositions of the alloys made, together with the nature of each addition agent. The chief sources of impurities are to be found in: (1) the copper used, (2) the alloying agents, (3) the crucible and flux materials, and (4) oxygen contamination from the air.

The copper used contained less than five hundredths of one per cent of total impurities, no single element occurring in a quantity greater than a few thousandths of one per cent; the addition agents, though usually less pure, were added in such small quantities that except in a few special cases no contamination in excess of one thousandth of one per cent could have been introduced in this way. New clay-graphite crucibles and a c.p. borax flux were employed. That no detectable contamination by metallic elements was introduced by the melting technique employed is indicated by the analysis of the blank alloy, number 82. Some oxygen undoubtedly was introduced into the melts both by the addition of tarnished metals and by contact with the air during casting. Almost all

TABLE 1.—*List of Alloys*

Alloy No.	Composition, Per Cent. Balance Copper	Addition Agent	Oxidation Behavior
15	0.045 Si	Technical silicon	Subscale forms
16	0.033 Mn	Technical manganese	Subscale forms
17	0.103 Si	Technical silicon	Subscale forms
18	0.084 Mn	Technical manganese	Subscale forms
19	0.076 Si	Technical silicon	Subscale forms
20	0.180 Si	Technical silicon	Subscale forms
22	0.858 Si	Technical silicon	Subscale spalls
23	0.30 Si	Technical silicon	Subscale forms
24	0.59 Si	Technical silicon	Subscale forms
25	1.93 Si	Technical silicon	Subscale spalls
26	0.22 Mn	Technical manganese	Subscale forms
27	0.42 Mn	Technical manganese	Subscale forms
28	0.42 Mn	Technical manganese	Subscale forms
29	1.00 Mn	Technical manganese	Subscale forms
30	0.64 Mn	Technical manganese	Subscale forms
31	1.55 Mn	Technical manganese	Subscale forms
32	0.03 P	Phosphor copper	Subscale forms
33	0.07 P	Phosphor copper	Subscale forms
34	0.105 P	Phosphor copper	Subscale forms
35	0.24 P	Phosphor copper	Subscale forms
36	0.42 P	Phosphor copper	Subscale melts below 1000°C.
37	0.002 P	Phosphor copper	External oxidation only
38	0.96 P	Phosphor copper	Subscale melts below 1000°C.
39	2.05 P	Phosphor copper	Subscale melts below 1000°C.
40	0.011 Al	Hoopes aluminum	External oxidation only
41	0.03 Al	Hoopes aluminum	Subscale forms
42	0.06 Al	Hoopes aluminum	Subscale forms
43	0.08 Al	Hoopes aluminum	Subscale forms
44	0.17 Al	Hoopes aluminum	Subscale forms
45	0.45 Al	Hoopes aluminum	Subscale forms
46	0.72 Al	Hoopes aluminum	Subscale forms
47	0.91 Al	Hoopes aluminum	Subscale forms
48	0.16 Zn	Cartridge brass	Subscale forms
49	0.05 Ti	Technical titanium	Subscale forms
50	0.11 Ni	Mond nickel	External oxidation only
51	0.10 Cr	Technical chromium	Subscale forms
52	0.14 Co	Rondells of cobalt	Subscale forms
53	0.10 Fe	Carbonyl iron	Subscale forms
54	0.02 Be	Beryllium copper	Subscale forms
55	0.10 Mg ^a	Distilled magnesium	Subscale forms
57	0.28 Cd	Technical cadmium	Subscale melts below 1000°C.
58	0.25 In	Technical indium	Subscale forms
59	0.16 Zr	Technical zirconium	Subscale forms
60	0.31 Sn	Straits tin	Subscale forms
61	Traces Ce	Technical cerium	Subscale forms
62	0.12 As	Technical arsenic	Results uncertain
63	0.34 Sb	Technical antimony	Results uncertain

TABLE 1.—(Continued)

Alloy No.	Composition, Per Cent. Balance Copper	Addition Agent	Oxidation Behavior
64	0.25 Cd	Copper cadmium alloy	Subscale melts below 1000°C.
65	0.03 Ga	Technical gallium	Subscale forms
68	0.49 Tl	Technical thallium	Results uncertain
69	0.45 Pb	Electrolytic lead	Results uncertain
71	0.04 Cb(max)	Sheet columbium	Subscale forms
72	0.04 Ta(max)	Sheet tantalum	Subscale forms
73	0.38 Bi	Electrolytic bismuth	Results uncertain
74	0.05 B ^a	Boron powder	Subscale forms
75	0.115 Ni	Mond nickel	Subscale forms
76	0.08 Cr	Technical chromium	Subscale forms
77	0.018 Be	Beryllium copper	Subscale forms
78	0.054 Be	Beryllium copper	Subscale forms
79	0.101 Be	Beryllium copper	Subscale forms
80	0.08 Be	Beryllium copper	Subscale forms
81	Traces Ca	Calcium turnings	Subscale forms
82	See note ^b	None	External oxidation only
83	0.10 Ba	Technical barium	Subscale forms
84	0.02 Li	Technical lithium	Subscale forms
85	0.03 Be + 9.52 Zn	As alloys 54 and 48	Double subscale
86	0.13 Al + 9.29 Zn	As alloys 40 and 48	Double subscale
87	0.085 Si + 9.81 Zn	As alloys 15 and 48	Double subscale
88	0.006 Be + 4.93 Sn	As alloys 54 and 60	Double subscale
89	0.06 Al + 5.43 Sn	As alloys 40 and 60	Double subscale
90	0.085 Si + 5.02 Sn	As alloys 15 and 60	Double subscale
91	0.21 Zn	Cartridge brass	Subscale forms
92	0.02 Be + 0.30 Sn	As alloys 54 and 60	Double subscale
93	0.003 Be + 0.049 Al	As alloys 54 and 40	Subscale forms
95	0.09 V	Vanadium copper	Subscale forms
98	0.02 S ^a	Roll sulphur	Results uncertain
99	0.1 Se ^a	Selenium stick	Subscale forms
100	0.1 Te ^a	Tellurium lump	Results uncertain
101	5 Ni ^a	Mond nickel	Subscale forms
102	1 Ag ^a	Technical silver	External oxidation only
103	0.03 Bi ^a	Alloy 73	External oxidation only
104	0.03 Sb ^a	Alloy 63	Subscale forms
105	0.03 As ^a	Alloy 62	Subscale forms
106	0.1 Sr ^a	Distilled strontium	Subscale forms
109	0.1 Pt ^a	Platinum wire	External oxidation only
110	0.0125 Be + 5 Sn ^a	As alloys 54 and 60	Double subscale
111	0.03 Pb ^a	Alloy 69	Subscale forms
112	0.03 Ti ^a	Alloy 68	Results uncertain
113	0.2 Pd ^a	Palladium sponge	External oxidation only
114	0.1 W ^a	Tungsten wire	Subscale forms
117	0.1 Na ^a	Technical sodium	Subscale forms
118	0.2 Ge ^a	Technical germanium	Subscale forms

^a Compositions so marked are nominal, all others by chemical analysis.

^b Reported as 99.953 per cent Cu with no impurity above the normal level for OFHC copper.

of the alloys exhibited small quantities of oxide inclusions, which doubtless formed during the melting and casting operations. By the examination of a blank sample, alloy 82, which failed under all treatments to exhibit internal oxidation, it was demonstrated that the total quantity of impurities that may have been introduced did not interfere with the subsequent experiments. Such effects as are reported, therefore, may be confidently ascribed to the presence of the intended additions rather than to impurities.

Heats of about 2000 grams were cast in an iron mold 12 by 2 by 1 in. washed with lime; the ingots were scalped all over to a depth of $\frac{1}{8}$ in. and were cold-rolled to a thickness of about $\frac{1}{4}$ in. From this material, oxidation samples $\frac{1}{2}$ in. square were cut. In order to standardize the surface condition, each sample was cleaned by grinding on 000 emery paper immediately before the oxidizing treatment. The initial thickness of each sample was measured.

Two different techniques were employed in carrying out the oxidation treatments. One consisted simply in heating in the air. The samples were set on edge on Sil-O-Cel bricks in a temperature-controlled electric muffle furnace. The second was, in effect, a bright anneal in an oxygen partial pressure equal to the decomposition pressure of cuprous oxide saturated with copper. To accomplish this the samples were packed in a mixture of equal parts of cuprous oxide and copper metal powder, enclosed in an iron pipe fitted with copper-foil gaskets. In a few special tests, to be described later, other oxides were substituted for the cuprous oxide and copper in order to attain lower oxygen pressures.

Specimens of all alloys were oxidized by each of the two methods at two temperatures, 1000° and 600°C. In addition, samples of the silicon, manganese, phosphorus and aluminum alloys were treated at two intermediate temperatures, 871° and 750°C. The time factor also was varied in a series of tests, but at least one sample of every alloy was run for 2 hr. at 1000°C., and one for 192 hr. at 600°C.

After the heat-treatment, each sample was sectioned across the center perpendicular to the broad face, mounted in Woods metal and polished by the usual methods. The etching solution used was the same for all alloys; namely, equal parts of ammonia, hydrogen peroxide 3 per cent solution, and water. A rather deep etch was usually required. During the early stages of metallographic preparation the zone of internal oxidation was sometimes evident in the sample, but in the finished polish before etching no trace of the oxide layer could be seen except in the alloys containing the largest quantities of the oxidizing element.

Survey of Binary Alloys

The alloys that exhibited internal oxidation under the conditions of these tests have been indicated in Table 1; among the binary combina-

tions so designated will be found those containing Al, Sb, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cb, Ga, Ge, In, Fe, Pb, Li, Mg, Mn, Ni, P, Se, Si, Na, Sr, Ta, Sn, Ti, W, V, Zn, and Zr. These elements possess the expected common characteristic that their oxides, whenever reliable data are available, are found to be more stable than cuprous oxide. Table 2 lists the free energies of formation of some of the more common oxides calculated from heat of formation and entropy data. These free-energy data may be taken as pertaining also to the formation of oxide from a solid solution, for the free energy of formation of solid solutions is of a minor order of magnitude.

With the exception of silver oxide, all of the oxides listed in the table have higher free energies of formation than cuprous oxide. The copper-silver alloy did not exhibit internal oxidation nor did the alloys containing platinum and palladium, whose oxides are also known to be very unstable.

Several of the alloying agents whose oxides occur above cuprous oxide in Table 2, or in all probability would do so if values were available, failed to give clear evidence of subscale formation, among them bismuth, sulphur, tellurium, and thallium. It may be that the cause of this behavior is to be found in an unfortunate choice of experimental conditions, for Blazey⁵ has reported evidence of internal oxidation in alloys containing bismuth.

TABLE 2.—*Free Energy of Formation of the Oxides*

Oxide	ΔF	Oxide	ΔF	Oxide	ΔF	Oxide	ΔF
V ₂ O ₅	397.1	SiO ₂	190.5	Sb ₂ O ₃	128.0	ZnO	70.0
Al ₂ O ₃	364.1	As ₂ O ₅	185.8	SrO	124.2	SnO	50.5
V ₂ O ₄	351.8	Sb ₂ O ₄	174.5	SnO ₂	122.2	CdO	48.5
V ₂ O ₃	300.0	WO ₃	172.4	As ₂ O ₃	115.4	FeO	46.2
MnO ₄	299.8	Fe ₂ O ₃	171.1	BaO	111.6	PbO	30.5
Cr ₂ O ₃	248.3	CaO	139.6	Pb ₃ O ₄	108.0	CuO	25.0
Fe ₃ O ₄	222.3	MgO	137.9	MnO ₂	105.3	Cu ₂ O	11.8
CeO ₂	210.9			Bi ₂ O ₃	96.1	Ag ₂ O	-30.9
Sb ₂ O ₅	191.9			MnO	78.2		

Photomicrographs of the subscales in a number of the alloys are exhibited in Figs. 6 to 12. Some of the oxidized zones are only faintly discernible, owing to the small quantity of the oxidizing element and the resultant small quantity of oxide in the alloy. In such samples the precipitation is usually heaviest near the limit of the zone of penetration. Although all of the samples represented have been oxidized under identical conditions of time and temperature, the differences in the widths of the subscale bands shown in the pictures may not be interpreted as



FIG. 6.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS.

Upper four pictures, magnification $\times 50$, are arranged with outside surface of sample at bottom and unoxidized alloy at top. Arrows indicate limit of internal oxidation. Lower four pictures show oxide precipitate in each subscale, magnification $\times 500$.

Cb—Alloy No. 71, 0.04 per cent Cb, heated 2 hours at 1000°C . in oxide pack. Outside surface of sample is not shown.

Al—Alloy No. 44, 0.17 per cent Al, heated 2 hours at 1000°C . in oxide pack.

Ba—Alloy No. 83, 0.10 per cent Ba, heated 2 hours at 1000°C . in oxide pack. Photographed in oblique light.

V—Alloy No. 95, 0.09 per cent V, heated 2 hours at 1000°C . in oxide pack.

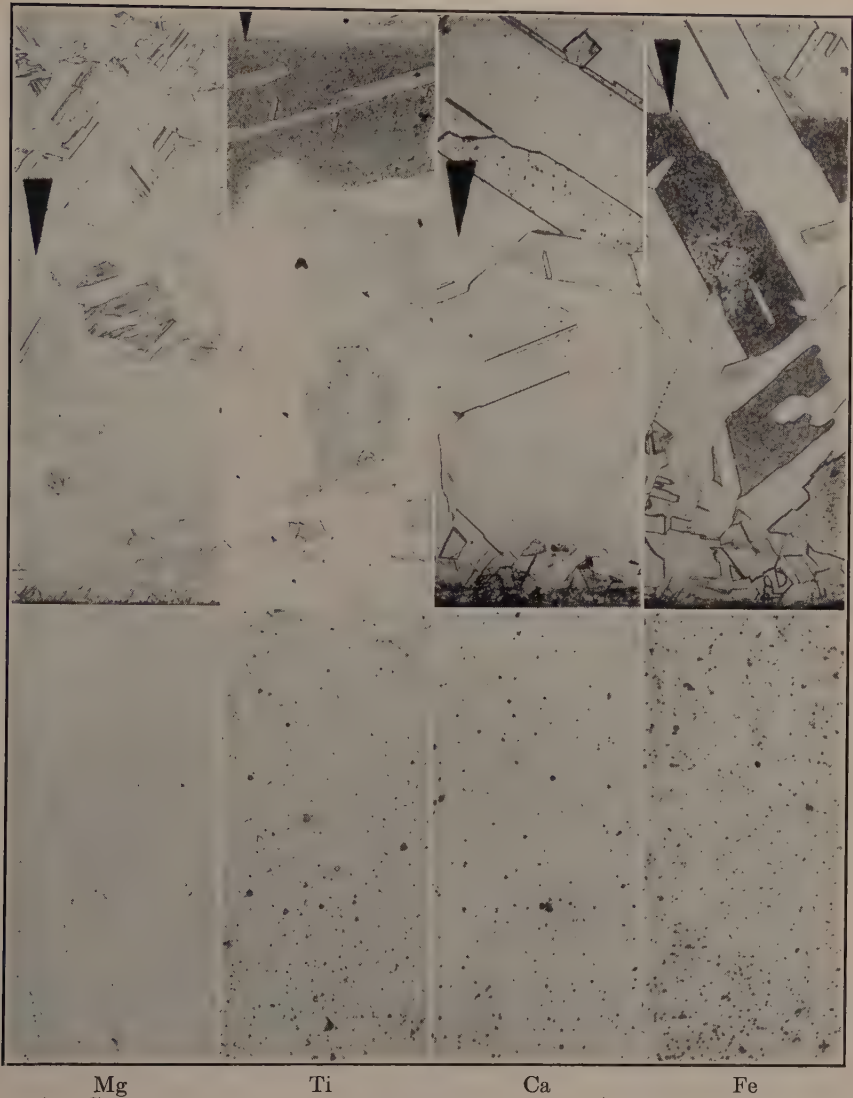


FIG. 7.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

Mg—Alloy No. 55, 0.1 per cent Mg (nominal), heated 2 hours at 1000°C. in copper oxide pack.

Ti—Alloy No. 49, 0.05 per cent Ti, heated 2 hours at 1000°C. in copper oxide pack. Outside surface of sample is not shown.

Ca—Alloy No. 81, "traces Ca," heated 2 hours at 1000°C. in copper oxide pack.

Fe—Alloy No. 53, 0.10 per cent Fe, heated 2 hours at 1000°C. in copper oxide pack.

indicating directly the relative rates of penetration of oxidation in the various alloy systems, because the concentrations differ widely from alloy to alloy and the rate of penetration necessarily varies with the concentration in any one system.

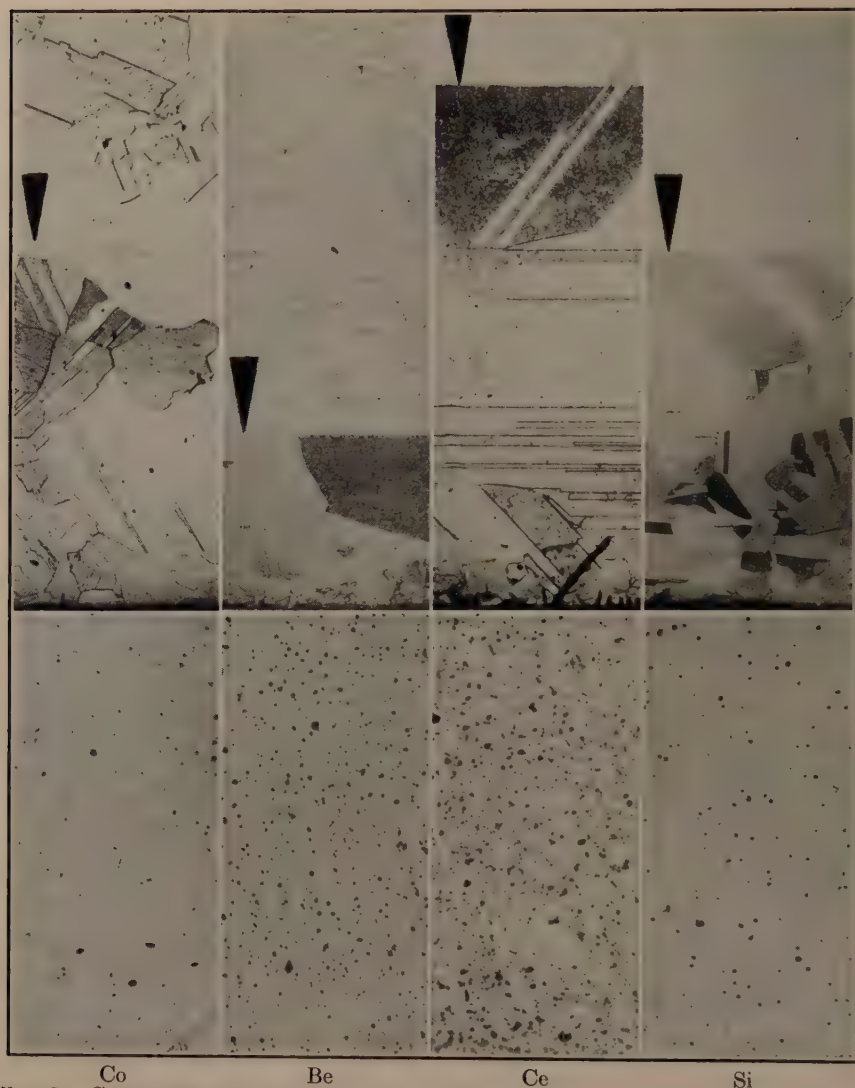


FIG. 8.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

Co—Alloy No. 52, 0.14 per cent Co, heated 2 hours at 1000°C. ($\times 50$ in the air) ($\times 500$ in copper oxide pack).

Be—Alloy No. 78, 0.054 per cent Be, heated 2 hours at 1000°C. in copper oxide pack.

Ce—Alloy No. 61, "traces Ce," heated 2 hours at 1000°C. in copper oxide pack.

Si—Alloy No. 19, 0.076 per cent Si, heated 2 hours at 1000°C. in copper oxide pack.

The limits of penetration are sharply marked by straight lines in most samples (Figs. 6 to 10). Exceptions to this observation are found chiefly among the alloys whose oxides form very coarse precipitates and among the alloys having a high concentration of the alloying element (Figs. 11 and 12). Evidently there is little if any anisotropy of diffusion of oxygen



FIG. 9.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

Zr—Alloy No. 59, 0.16 per cent Zr, heated 2 hours at 1000°C. in copper oxide pack. Photographed in polarized light.

Mn—Alloy No. 27, 0.42 per cent Mn, heated 2 hours at 1000°C. in copper oxide pack.

Cr—Alloy No. 76, 0.08 per cent Cr, heated 2 hours at 1000°C. in copper oxide pack.

W—Alloy No. 114, 0.1 per cent W (nominal), heated 2 hours at 1000°C. in copper oxide pack. Photographed in oblique light.

in copper under these conditions, for otherwise a more rapid advance of the oxidation in certain grains of the alloy should be expected.

It will be noted also that the presence of the precipitate is often more evident in certain grains of the metal than in their neighbors, see espe-

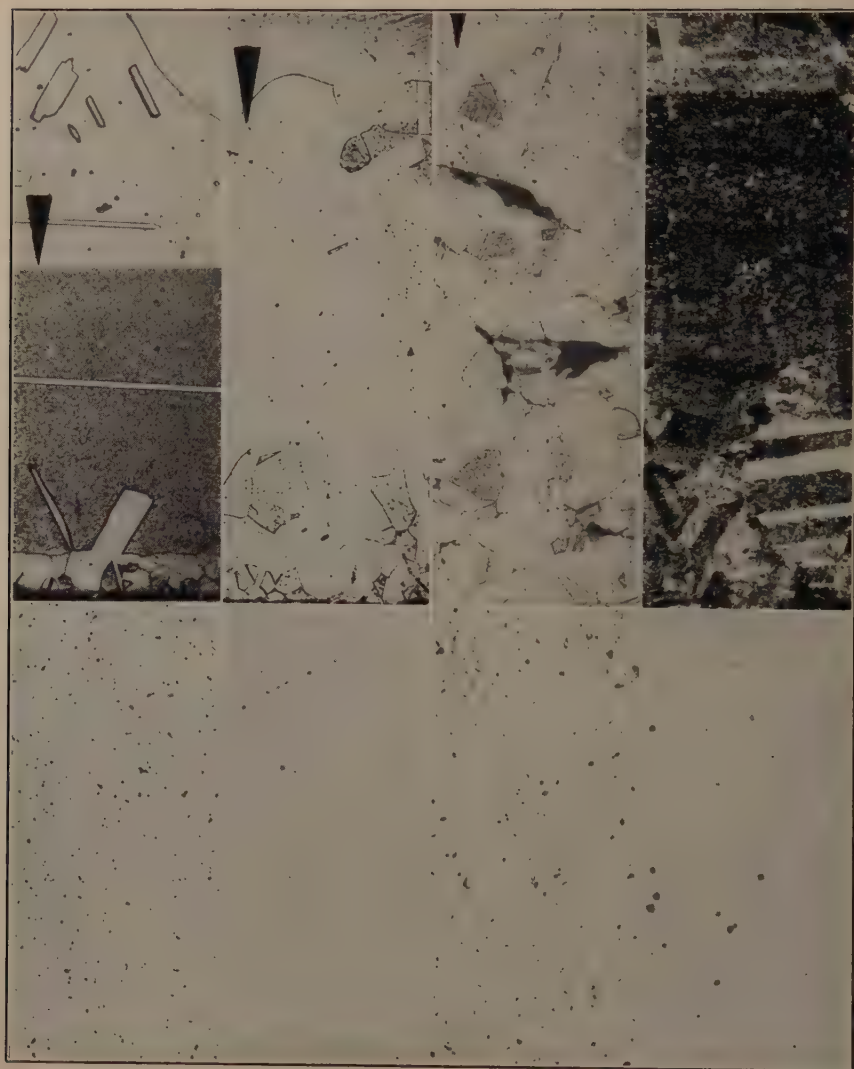


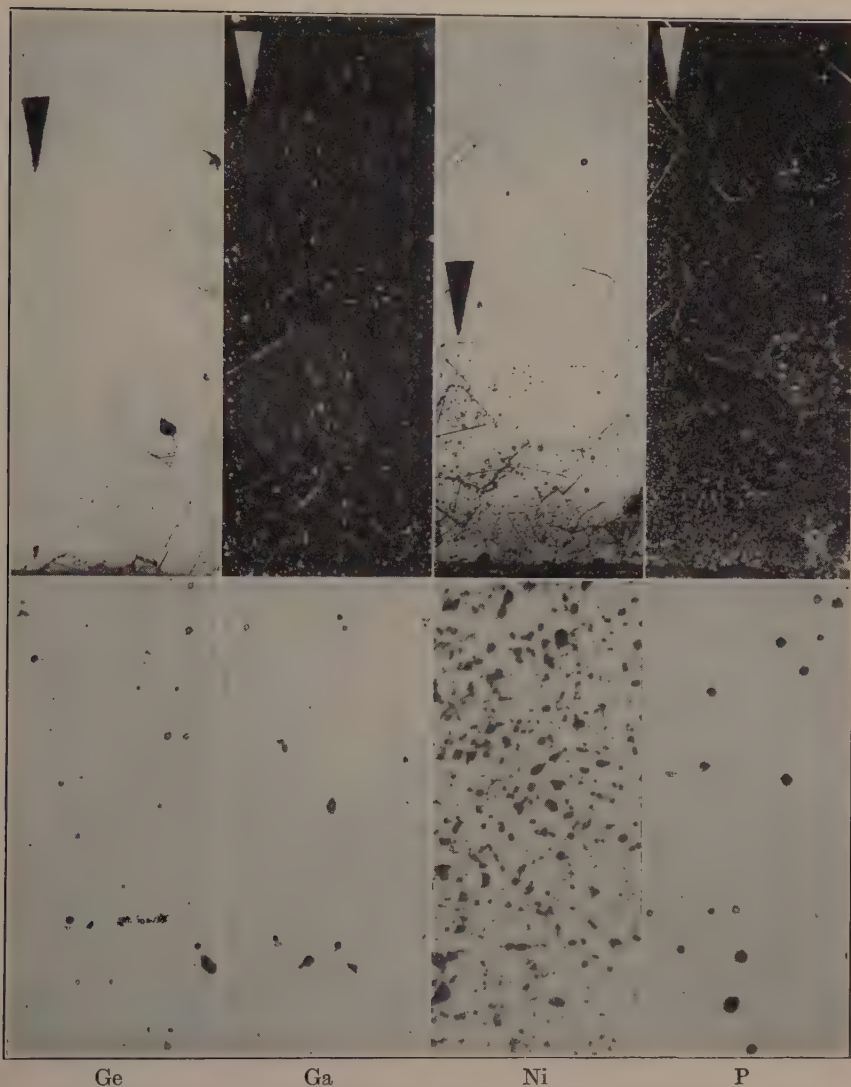
FIG. 10.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

Li—Alloy No. 84, 0.02 per cent Li, heated 2 hours at 1000°C. in copper oxide pack.

B—Alloy No. 74, 0.05 per cent B (nominal), heated 2 hours at 1000°C. in copper oxide pack.

Se—Alloy No. 99, 0.1 per cent Se (nominal), heated 2 hours at 1000°C. in copper oxide pack. Outside surface of sample not shown.

Ta—Alloy No. 72, 0.04 per cent Ta, heated 2 hours at 1000°C. in copper oxide pack. Photographed in oblique light.



Ge Ga Ni P
FIG. 11.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

Ge—Alloy No. 118, 0.2 per cent Ge (nominal), heated 2 hours at 1000°C. in copper oxide pack.

Ga—Alloy No. 65, 0.03 per cent Ga, heated 2 hours at 1000°C. in copper oxide pack. Photographed in polarized light; outside surface not shown.

Ni—Alloy No. 101, 5 per cent Ni (nominal), heated 2 hours at 1000°C. in copper oxide pack.

P—Alloy No. 32, 0.03 per cent P, heated 2 hours at 1000°C. in copper oxide pack. Photographed in polarized light.

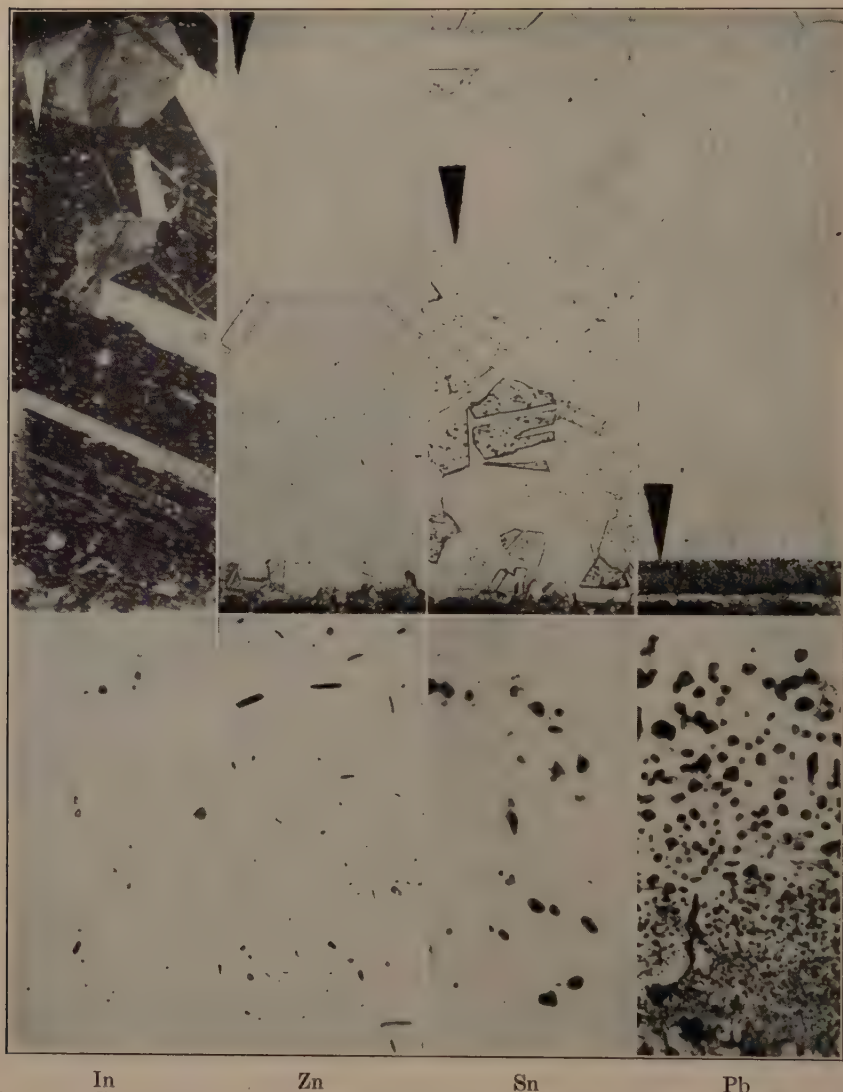


FIG. 12.—CROSS SECTION OF SUBSCALE IN FOUR ALLOYS. ARRANGEMENT DESCRIBED UNDER FIG. 6.

In—Alloy No. 58, 0.25 per cent In, heated 2 hours at 1000°C. in copper oxide pack. Photographed in polarized light.

Zn—Alloy No. 91, 0.21 per cent Zn, heated 2 hours at 1000°C. in copper oxide pack.

Sn—Alloy No. 60, 0.31 per cent Sn, heated 2 hours at 1000°C. in copper oxide pack.

Pb—Alloy No. 111, 0.03 per cent Pb (nominal), heated 2 hours at 1000°C. in copper oxide pack.

cially Fig. 2. This is purely an orientation etching effect. A careful examination of a number of such cases has revealed no difference in the size or quantity of the precipitate in adjacent grains exhibiting this difference in shade.

Size and Shape of the Oxide Particles

The individual photographs of Figs. 6 to 12 have been arranged in the order of the apparent particle sizes of the oxides. Referring again to Table 2, the order of the particle sizes is found to correspond very roughly with the order of the free energies of formation, the highest energy being associated with the smallest particle size. A number of the alloys are out of place in this sequence, but the general trend is unmistakable. In several instances where one of several oxides may have formed and the true one has not as yet been identified—for example, in the case of alloy 53 where there is a choice among FeO , Fe_2O_3 , or Fe_3O_4 —it is necessary arbitrarily to select one of the group to make the alloy assume its proper place. Unfortunately, data are available for only one or two of several possible oxides in a number of instances, thus further limiting the comparison. It should be pointed out also that the particle size is subject to several experimental variables to be discussed presently, and that one of these—namely, concentration—has been fixed only in the sense that all of the alloys are very dilute. Some deviation from a regular behavior may be anticipated on this account.

Although this relationship may be accidental, the number of cases in which it obtains is suggestive of the operation of a common principle. The final size of a particle of a newly formed phase may be considered as determined by the initial nucleus size, the rate of nucleation, and the rate of growth. Evidently the rate of growth in the present type of reaction is great, for the oxide particles near the metal-subscale interface are about as large as those near the metal-gas interface.

The initial nucleus size will affect the final size only in the sense that the larger nuclei will have an initial advantage in size over the smaller nuclei, but since nuclear sizes are very small compared with the sizes of the particles considered here,¹⁶ the effect is probably unimportant. The rate of nucleus formation, however, may be all important in determining the final particle size, for when many nuclei form, relatively less potentially precipitable solute remains available for the growth of each particle. Nucleation theory states that the minimum size of the stable nucleus should be the smaller the greater the free energy change accompanying the formation of the new phase;¹⁷ the smaller the minimum size, the greater the number of nuclei that can form, i.e., the greater the rate of nucleation. Thus a precipitation reaction accompanied by a large change in free energy should form many small nuclei with small opportunity for further growth; i.e., should furnish a small final particle size, which is consistent with the relationship observed. This argument is very tenuous when used, as it is here, to compare the behavior of different systems in which the factors determining nuclear sizes and rates may vary sensibly.

The size of the precipitate is also a function of the temperature of formation and of the concentration of the alloy. At high temperatures larger particles appear than at low temperatures (Fig. 13). This condition prevails in all of the alloys that were examined.

Low concentrations of the alloying element seem to favor a small particle size. Only a few systems have as yet been examined over a concentration range, but all of these showed this behavior. The effect is pronounced (Fig. 14), and the reasons for it are not altogether clear; it is possible that it is caused by a slower rate of growth in the more dilute alloy, owing to the flatter diffusion gradient.

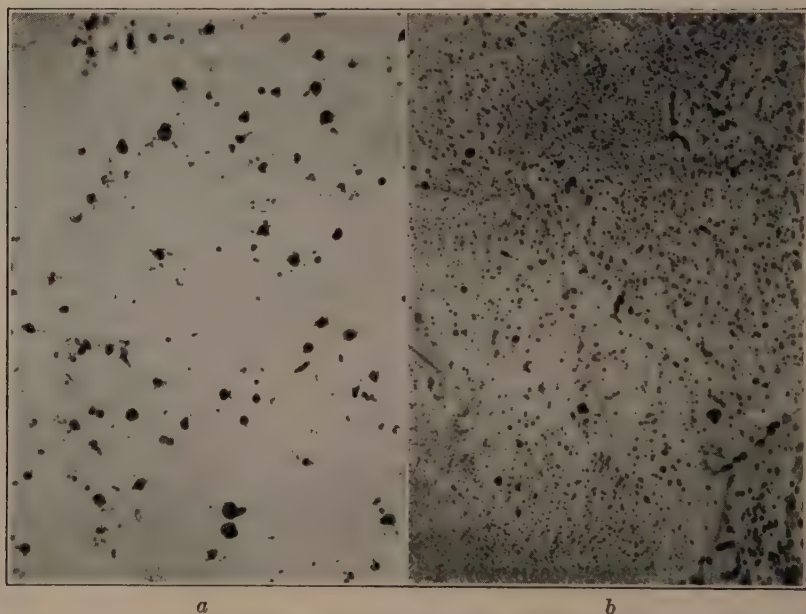


FIG. 13.—ALLOY OF 0.16 PER CENT ZINC OXIDIZED (a) AT 1000°C. AND (b) AT 600°C
× 500.

Shows increase in particle size of oxides as temperature of oxidation increases.

It might be expected that there would be a decrease in the particle size from the outside surface inward because of a continuing growth and agglomeration of the first-formed precipitates. Evidence of agglomeration was found in only a few samples, such as Pb in Fig. 12 and in some alloys containing Be (Fig. 19b). In most cases no extensive difference in the size of the particles within a single subscale was found. Apparently, because of the low solubility of the oxides in copper, the precipitate normally grows to its ultimate size almost immediately while it is still at the reaction front and does not thereafter agglomerate to any marked extent. This does not exclude the possibility of spheroidization, which seems to be common.



FIG. 14.—COPPER-SILICON ALLOYS OXIDIZED 2 HOURS AT 1000°C. $\times 500$. Shows increase in particle size of oxide as concentration of silicon increases. (See also Fig. 25.) Percentage of silicon as follows:

<i>a</i> , 0.045	<i>d</i> , 0.18	<i>f</i> , 0.59
<i>b</i> , 0.076	<i>e</i> , 0.30	<i>g</i> , 0.85
<i>c</i> , 0.103		

Because of their small size, the shapes of the particles ordinarily could not be observed with any confidence. Most of them appeared round, but where coarser precipitates occurred they sometimes seemed to have rectangular cross sections, as though they were platelike or acicular in form. Perhaps the finer precipitates tend to spheroidize after

formation and lose their characteristic forms more rapidly than do the coarser ones. Whatever its cause may be, this condition provides a definite obstacle to the observation of the Widmanstätten patterns which, according to the general principle stated by Mehl and Smith,¹⁸ should be expected in structures of this kind. In a few samples definite Widmanstätten patterns are to be found (Fig. 15). Groups of parallel

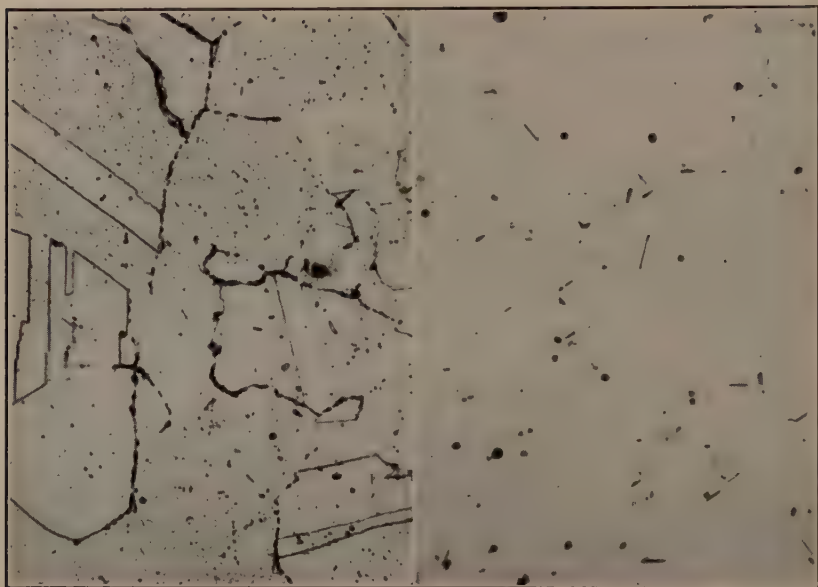


FIG. 15.—WIDMANSTÄTTEN PATTERNS IN SUBSCALE. $\times 500$.
a, 0.25 per cent In alloy oxidized at 600°C.
b, 0.16 per cent Zn alloy oxidized at 1000°C.

precipitate particles in these pictures are easily seen. The configurations shown are evidently complex and have not been analyzed.

Distribution of Oxide Particles

The increased particle count of the subscale bands near the front of reaction in a substantial fraction of the examples of Figs. 6 to 12 has already been pointed out. This state of affairs is in conflict with the prediction of the phase diagram, as is demonstrated in Fig. 16. Applying the lever principle to points on the composition line GZ within the field of $XO + \alpha$, the subscale zone, it is found that at the point *b* of intersection with the lever *abc*, which represents a point near the outside edge of the subscale, the ratio of XO precipitate to α solid solution is ba/cb . At point *e* on the lever *def*, which corresponds to a point near the inside edge of the subscale, the oxide to metal ratio is de/ef . Obviously ba/cb is larger than de/ef , but the opposite effect is observed in some of the photographs where the oxide is most plentiful next to the unoxidized solid solution.

tend to overtake the rate of delivery of the oxygen, thereby decreasing the rate of advance of the reaction zone and increasing the total quantity of oxide formed at each step in the advance. Exceptions to this behavior

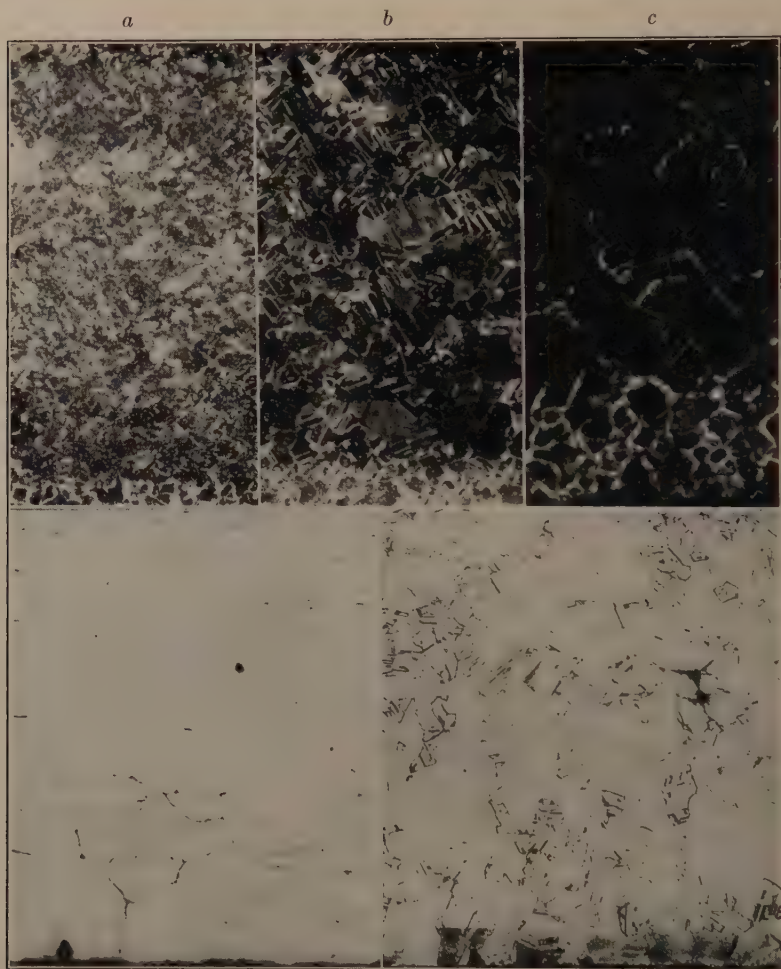


FIG. 18.—COPPER ALLOYS OXIDIZED AT 600°C. $\times 50$.
a, 0.02 per cent Be. Photographed in polarized light.
b, 0.25 per cent In. Photographed in polarized light.
c, 0.1 per cent Mg. Photographed in polarized light.
d, 0.06 per cent Al. Photographed in bright field.
e, 0.16 per cent Zn. Photographed in bright field.

may, upon this basis, be explained as instances of a very slow diffusion of the metallic element.

The structures discussed thus far have been formed at the relatively high temperature of 1000°C. At 600°C. a remarkable difference is

found in the distribution of the oxide in a large number of the alloys. The oxide particles, instead of being deposited with apparent disregard for the matrix grains and grain boundaries, as they are at the higher temperature, occur in high concentration along the boundaries. Moreover, in many cases, the matrix grain boundaries contain oxide particles to a depth far in advance of the principal front of reaction. This may be caused by a more rapid diffusion of oxygen along the grain boundaries than through the mass of the grains at this low temperature. A series of photomicrographs illustrating this behavior is assembled in Fig. 17. These depict the structure of a copper-silicon alloy oxidized at four temperatures: 1000°, 871°, 750° and 600°C. The sample treated at 1000°C. shows no heavier precipitation at the grain boundaries than elsewhere. A treatment at 871°C. produces a structure in which the grain boundaries are lightly but definitely delineated by a precipitate. At 750°C. the grain boundaries are heavily outlined with oxide out to the general front of reaction and at 600°C. the deposits along the boundaries extend far ahead of the main reaction front.

Some alloys failed to exhibit such extreme differences at the various temperatures of reaction, but all showed preferential precipitation at the grain boundaries when oxidized at 600°C. A group of pictures illustrating several degrees of this effect is presented in Fig. 18.

A similar relationship between transcrystalline and grain-boundary diffusion has been reported in the diffusion of thorium through tungsten,¹⁹ but the differences were not so great as in some of the present examples. It is altogether reasonable that the difference in the behavior of the grain boundary and of the body of the crystal should become less marked at elevated temperatures because the excess energy content of the boundary should become relatively less important as the total energy content of the system increases.

Liesegang Bands

In certain of the alloys there occurred a special type of distribution of the oxide particles in a series of layers (Fig. 19). This configuration has been identified by C. S. Smith⁷ as an instance of Liesegang ring formation and does, indeed, closely resemble the familiar structure of that name found in gels containing a soluble salt and within which a precipitate has been formed by the inward diffusion of a suitable precipitating reagent. In the literature of the subject there are recorded a number of fundamentally different explanations of the phenomenon, none of which seems to have been accorded general acceptance. Among them the one that appears most satisfactory for the present case is based upon the assumption that nucleation may proceed only in the presence of a significant degree of supersaturation of the reacting elements in the solvent. Thus a line of nuclei once formed is permitted to grow through the

consumption of the dissolved alloying element considerably in advance of the reaction zone and further nucleation is possible only in a front well ahead of the previous position where the requisite degree of supersaturation can once more be attained. The process repeating itself at intervals in this way deposits the oxide in a series of layers.

Evidence that the extraction of the alloying metal is proceeding far ahead of the reaction zone is provided by Fig. 19*a*, where a marked increase in the grain size appears to be occurring before the advancing oxide precipitation. This growth is probably induced by the strains set up as a result of the changing of the lattice dimensions of the solid

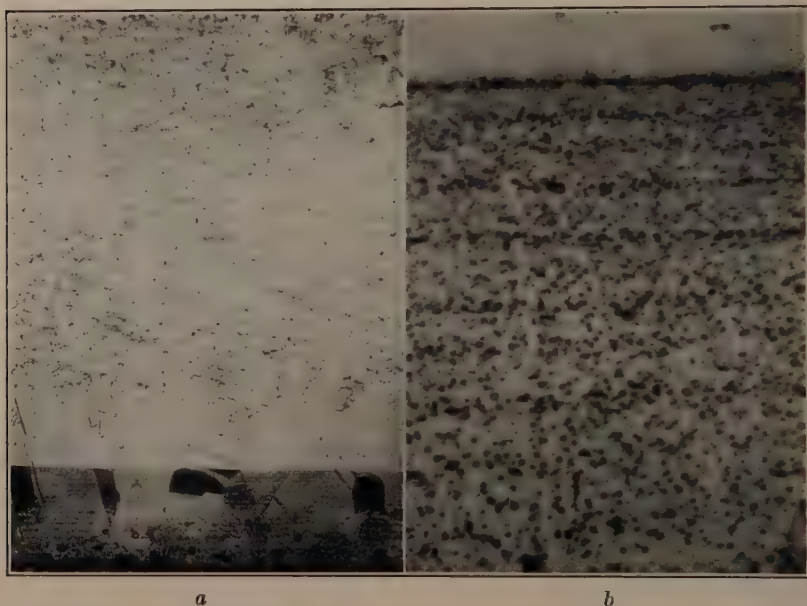


FIG. 19.—ALLOY OF 0.106 PER CENT BERYLLIUM OXIDIZED 2 HOURS AT 1000°C. *a*, $\times 50$; *b*, $\times 500$.
Shows Liesegang bands in subscale zone.

solution when beryllium is removed. A somewhat similar grain growth resulting from the diffusion of zinc into copper has been observed.²⁰

Varied aspects of the same behavior are illustrated in Figs. 20 and 21. The copper-aluminum alloy of Fig. 20 presents an almost pearlitic appearance. Upon close inspection the oxide lamellae are seen to be broken at frequent intervals. No doubt the oxide laid down in this form does provide a very significant obstacle to the diffusion of oxygen, for the reaction front of Fig. 21*a* shows definite signs of blocking its own further growth. This structure is shown in greater detail in Fig. 21*b*. Here it is clearly seen that the silica is first deposited in a solid film, which later breaks up and spheroidizes, admitting the passage of oxygen. Sometimes subscales of this type spall, cleaving away from the unoxidized

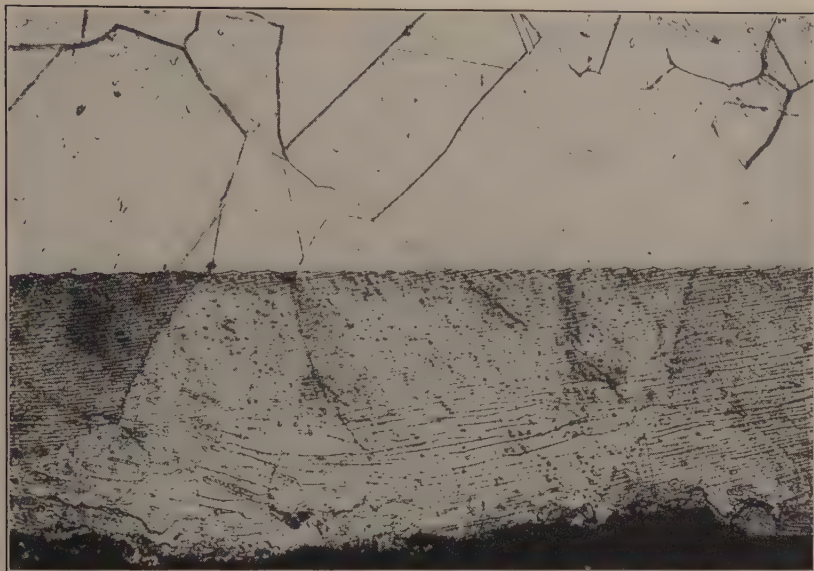


FIG. 20.—ALLOY OF 0.72 PER CENT AL OXIDIZED 2 HOURS AT 1000°C. $\times 230$.
Pearlitic structure in subscale may be Liesegang bands; that is, a rhythmic precipitation of Al_2O_3 in copper.

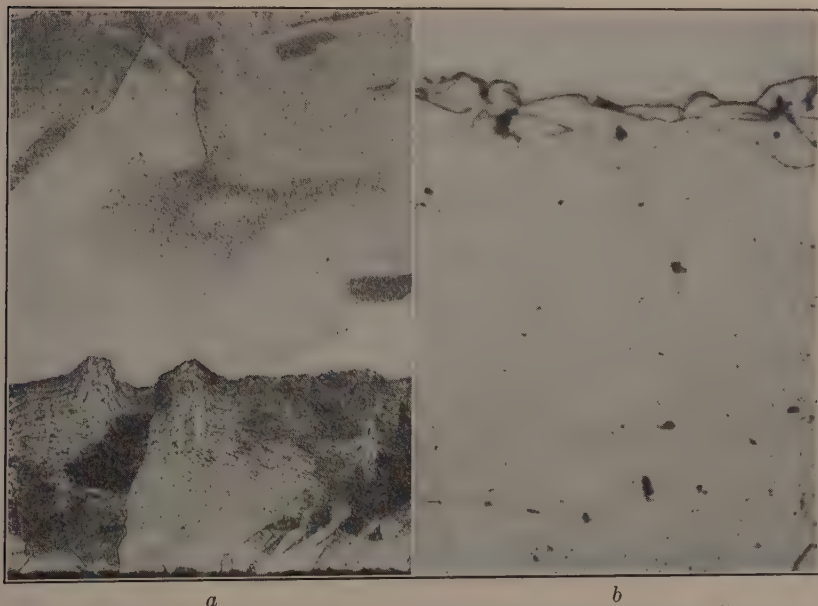


FIG. 21.—ALLOY OF 0.180 PER CENT SILICON OXIDIZED 4 HOURS AT 1000°C. *a*, $\times 50$
b, $\times 500$.

Shows structure resembling Liesegang bands which appear to be partially destroyed by spheroidization as oxidation proceeds.

metal along the line of continuous precipitation (see Fig. 25g). Liesegang bands were identified only in alloys containing aluminum, beryllium and silicon. The markings were most distinct in the alloys of higher concentrations which were oxidized at high temperatures.

Rate of Growth of Subscale

Although the present experiments were not designed for a quantitative study of the rate of growth of the subscale, it is possible to draw from them several conclusions of a general nature concerning the qualitative influence of some factors upon the rate of growth. Among the variables that may be expected to exercise an important influence are: (1) the time during which oxidation has operated, (2) the concentration of the alloy, (3) the rate of the inward diffusion of oxygen, (4) the rate of the outward diffusion of the alloying element, (5) the stoichiometric proportions of oxygen and the metal in the oxide, (6) the temperature of oxidation and (7) the oxygen pressure at the surface of the sample.

The velocity of the penetration of oxidation decreases with time, as is to be expected of a diffusion process in which the distance of transport of one of the reacting elements, in this case oxygen, is increasing. Within the first few minutes of oxidation the rate of growth of the subscale is very rapid (Fig. 22). A group of samples of an alloy containing 0.103 per cent Si was heated for a series of time intervals in air at 1000°C. After 3 min. of heating, the first sample removed from the furnace was found

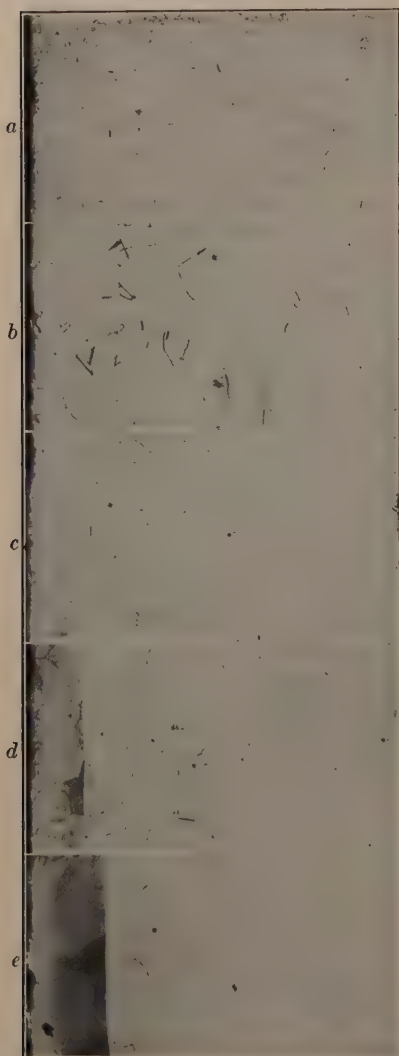


FIG. 22.—ALLOY OF 0.103 PER CENT SILICON HEATED IN AIR AT 1000°C. $\times 50$.

Shows rapid rate of growth of subscale in early stages of oxidation. (See also Fig. 23.)

- a, heated 3 minutes.
- b, heated 4 minutes.
- c, heated 5 minutes.
- d, heated 10 minutes.
- e, heated 20 minutes.

not to have reached the furnace temperature, as was indicated

by the absence both of internal oxidation and of complete recrystallization. One minute later, when the next sample was removed, a subscale of appreciable thickness was found and in another minute its depth had

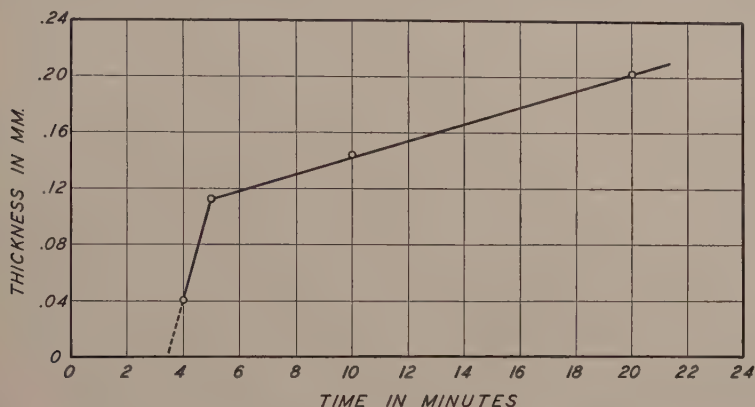


FIG. 23.—GRAPHIC REPRESENTATION OF RATE OF GROWTH OF SUBSCALE IN ALLOY OF FIG. 22.



FIG. 24.—ALLOY OF 0.103 PER CENT SILICON OXIDIZED AT 1000°C. IN COPPER-COPPER OXIDE PACK. $\times 50$.

Illustrates growth of subscale with time.

a, heated 1 hour.

b, heated 2 hours.

c, heated 4 hours.

d, heated 8 hours.

been nearly doubled. The nature of this effect is perhaps more readily understood from the plot of Fig. 23, where the penetrations measured in Fig. 22 are plotted as a function of time.

The high initial rate of subscale formation may be a matter of considerable technical importance, for it indicates that an annealing treatment under oxidizing conditions can hardly be so short as to avoid internal oxidation. Another group of pictures showing the rate of growth of the band of internal oxidation in the same alloy treated for longer time intervals in the copper oxide pack is presented in Fig. 24.

As the concentration of the alloy increases, the rate of penetration of the oxidation decreases (Fig. 25). A direct proportionality between the concentration and the time required to produce a subscale of a given thickness should be expected if all other variables could be held constant, for, if the diffusion velocity of oxygen were fixed, the quantity delivered to the reaction front and, hence, the quantity of the alloying element oxidized, would be directly proportional to the time. Experimentally it is not possible to control the diffusion rates of either oxygen or the alloying element, both of which change somewhat as the concentration of the alloy is varied. The results of a typical test in which three copper-silicon alloys were internally oxidized to a common depth at a temperature of 871°C. are given in Table 3.

TABLE 3.— <i>Copper-silicon Alloys Internally Oxidized</i>	
ALLOY CONCENTRATION, WEIGHT PER CENT Si	HOURS TO REACH THICKNESS OF 0.045 MM. AT 871°C.
0.180	8
0.103	4
0.045	2

Over the range covered the agreement with the predicted behavior is reasonably good. There is a small deviation in the direction of a retardation of the rate as the concentration increases; either a lowering of the rate of delivery of oxygen to the interface or an increase in the rate of delivery of silicon to the interface or both operating together could account for the effect as discussed below.

It is obvious that a small quantity of oxygen in addition to that consumed in the oxidation reaction will be required to saturate the copper in the subscale, and that this quantity should be approximately the same in alloys of all concentrations. Even at high temperatures, where the oxygen solubility is the greatest, the amount required for this function will be very small compared with that involved in oxidation.*

Since oxygen in passing from the surface of the sample to the zone of reaction travels through copper impoverished in the solute metal by the precipitation of the oxide, it might be expected that the delivery rate of the oxygen would be independent of the alloy concentration. Possibly

* Taking 0.015 per cent as the solubility of oxygen at 1050°C., and assuming the oxidation of a copper-silicon alloy containing 0.1 per cent Si, the distribution of the oxygen would be 0.0015 grams per c.c. dissolved in the copper and 0.1053 grams per c.c. as SiO₂. At lower temperatures the quantity of dissolved oxygen would be much lower.

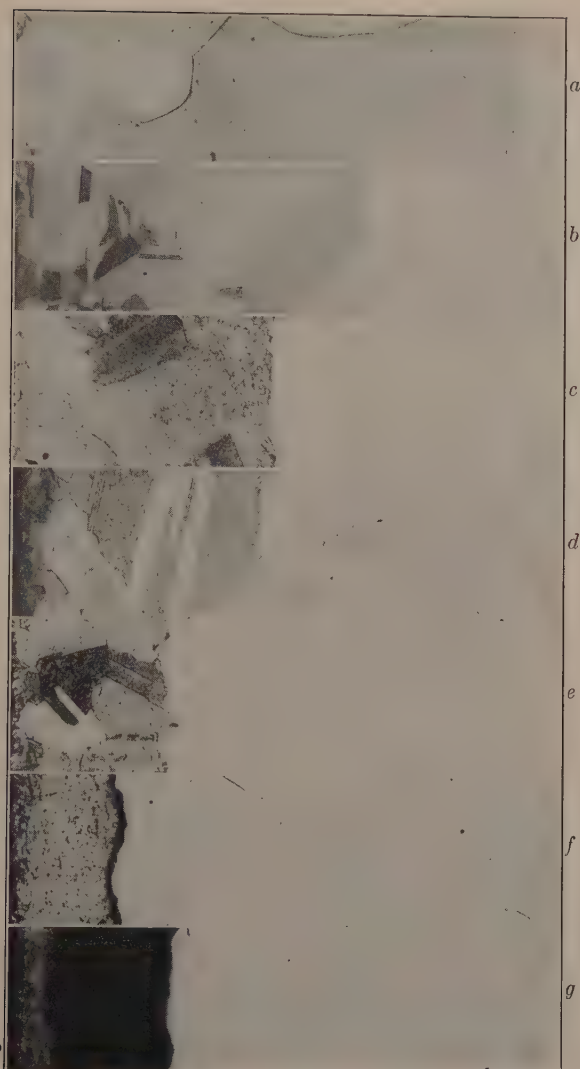


FIG. 25.—COPPER-SILICON ALLOYS OXIDIZED 2 HOURS AT 1000°C. $\times 50$.
Shows decrease in rate of growth of subscale as silicon concentration increases.
(See also Fig. 14.) Percentage of silicon as follows:

<i>a</i> , 0.045	<i>e</i> , 0.30
<i>b</i> , 0.076	<i>f</i> , 0.59
<i>c</i> , 0.103	<i>g</i> , 0.85
<i>d</i> , 0.180	

at low concentrations this is approximately true, but at higher concentrations of the solute the precipitated oxide must provide a significant barrier to oxygen diffusion (Fig. 21).

The rate of delivery of the alloying element to the interface necessarily will increase with the concentration of the alloy as a result of the greater

diffusion gradient. This will have the effect of retarding the penetration of oxidation, because, with more of the oxidizing element delivered to the zone of reaction, more oxygen will be required to complete the precipitation at each step in the advance. Various elements diffuse through copper at different rates and the importance of the effect in various systems differ accordingly. A close relationship between the stoichiometric proportions of the oxide formed and the rate of the subscale growth seems necessary; twice as much oxygen is required to produce a formula weight of SiO_2 as would be needed to produce a formula weight of MgO , and the time to form a given thickness of subscale, accordingly, should be twice as long for the silicon alloy. The data available at present have failed to verify this relationship, but they are too few to provide an adequate test in which all other variables are held constant.

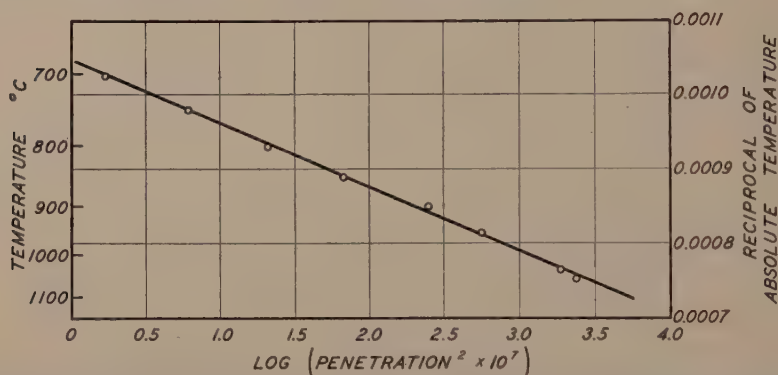


FIG. 26.—REPLOTTING OF DATA OF C. S. SMITH, SHOWING RELATIONSHIP BETWEEN PENETRATION AND TEMPERATURE OF OXIDATION FOR AN ALLOY OF 0.103 PER CENT SI. PENETRATION IS MEASURED IN MILLIMETERS.

Duration of heat-treatment, 2 hours.

The rate of growth of the subscale increases rapidly with rising temperature, as may be seen by reference to Fig. 17. C. S. Smith has measured this effect in a copper alloy containing 0.103 per cent Si and has published a curve. If his data are replotted with one axis the reciprocal of the absolute temperature and the other the log of the penetration squared, a straight-line relationship results (Fig. 26). This behavior is precisely of the type to be expected of a diffusion process operating in accordance with Fick's law, where the log of the diffusion coefficient is a linear function of the reciprocal of the absolute temperature and the square of the distance is proportional to the diffusion coefficient.

At low temperatures some confusion in the measurement of the depth of the subscale arises because of the increasing dominance of grain-boundary penetration. Two separate rates of oxidation may then be measured: one the progress of the transcrystalline front of reaction and the other the limit of oxidation along grain boundaries. Since a transfer of oxygen from the boundaries into the grains and vice versa is certain to

occur, neither of these rates may be wholly separated from the other; the grain-boundary penetration will be smaller and the transcrystalline penetration greater than if the two could be isolated.

The effect of the oxygen pressure upon the rates of internal oxidation has not yet been studied at any length. It is to be anticipated that the further the oxygen pressure is lowered below the decomposition pressure of cuprous oxide, the slower will be the penetration, because with a lower concentration head of oxygen the diffusion gradient will be less steep. At a pressure equal to or below the decomposition pressure of the oxide of the alloying element, the reaction will cease altogether. Oxygen pressures above the decomposition pressure of cuprous oxide can be expected to affect the rate only to the extent that the quantity of oxygen in solution in the cuprous oxide surface scale is increased.

In a single experiment a copper-tin-beryllium alloy was heated in a mixture of copper-tin powder and stannous oxide instead of in the usual mixture of copper and copper oxide. The rate of formation of the beryllium oxide was here very much slower than when treated under the usual conditions. Because of the lower decomposition pressure of stannous oxide the oxygen pressure operating in this case was much lower than that provided by cuprous oxide.

Internal Oxidation in Ternary Alloys

Ternary-alloy behavior under conditions of internal oxidation is of special interest both from a scientific and a practical point of view, because the majority of the technically important alloys are of ternary or higher order systems. Photographs of the subscale appearing in several such alloys are presented in Figs. 27, 28 and 29. The copper alloys containing tin or zinc with aluminum, beryllium or silicon all show two distinct subscale zones. The oxides of both of the alloying elements occur in the outer band while only one of the oxides appears in the inner band. Thus there are, in effect, two subscales overlapping with one protruding farther into the sample than the other. Only one subscale zone can be seen in the alloy of copper-aluminum-beryllium (Fig. 29).

In general, it is to be expected that two separate reaction fronts should occur, because the lower limit of oxygen concentration at which the various oxides form will usually be different (Fig. 30). The minimum oxygen pressure for reaction is not a constant of the alloy system, but depends upon the concentration of the alloy and the temperature as well. Hence, it is to be expected that the order in which the oxides occur and the relative widths of the two subscale bands will change with the concentration of the alloy. This effect may be seen in a comparison of Figs. 31 and 28a. In the former alloy the tin to beryllium ratio is about 15, while in the latter it is 820, and the band of tin oxide, the coarser precipitate, is relatively much narrower in the first than in the



FIG. 27.—TERNARY ALLOYS OXIDIZED FOR 2 HOURS AT 1000°C. $\times 500$.

Band of coarse particles is three-phase subscale of zinc oxide with more stable oxide and copper. Second subscale is narrow band of fine precipitate at top of each picture. White band at bottom may be result of dezincification.

a contains 9.52 per cent Zn + 0.03 per cent Be.

b contains 9.24 per cent Zn + 0.13 per cent Al.

c contains 9.81 per cent Zn + 0.085 per cent Si.

second. At some particular concentration of the alloy the widths of the two subscale zones may become equal and appear as one (Fig. 29).

As with the less complex alloys, it is possible by means of phase diagrams to obtain a more comprehensive view of the modes of behavior to be expected of the ternary alloys. The diagram, including oxygen,

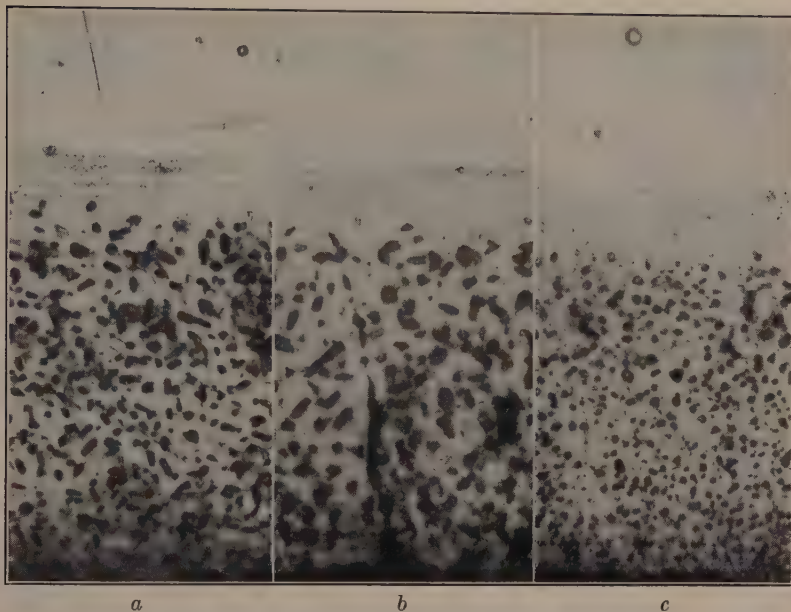


FIG. 28.—TERNARY ALLOYS OXIDIZED FOR 3 HOURS AT 900°C. $\times 500$.

There are two subscales: (1) a band of coarse particles of tin oxide with fine particles of other oxide in lower half of picture, and (2) a band of fine particles of second oxide near top of picture.

a contains 4.93 per cent Sn + 0.006 per cent Be.

b contains 5.43 per cent Sn + 0.06 per cent Al.

c contains 5.02 per cent Sn + 0.085 per cent Si.



FIG. 29.—ALLOY OF 0.003 PER CENT BERYLLIUM AND 0.049 PER CENT ALUMINUM OXIDIZED 2 HOURS AT 1000°C. $\times 50$.
Shows but a single zone of subscale.

is now of the quaternary class. A simplified three-dimensional isotherm is represented by its external fields only in Fig. 32*a*. Even the simplest

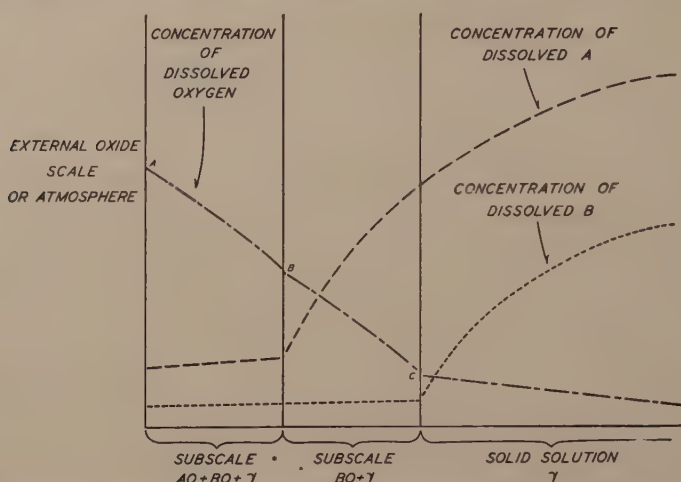


FIG. 30.—SCHEMATIC REPRESENTATION OF CONCENTRATIONS OF DISSOLVED OXYGEN AND TWO SOLUTE METALS IN TERNARY ALLOY UNDERGOING INTERNAL OXIDATION.

Element A will oxidize down to an oxygen concentration of b , but element B continues to oxidize until oxygen concentration reaches lower value c .

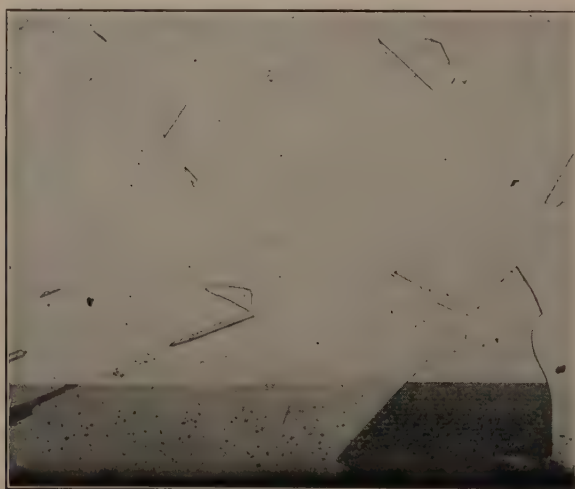


FIG. 31.—ALLOY OF 0.30 PER CENT TIN + 0.02 PER CENT BERYLLIUM OXIDIZED FOR 2 HOURS AT 1000°C. $\times 50$.

Shows double band of sparsely distributed tin oxide plus much beryllium oxide next to surface and zone of beryllium oxide alone next to unoxidized metal. Upper band is proportionally much wider than in Fig. 28*a*.

diagram of this kind is too complex for easy interpretation and to further simplify the discussion a two-dimensional section has been taken (Fig.

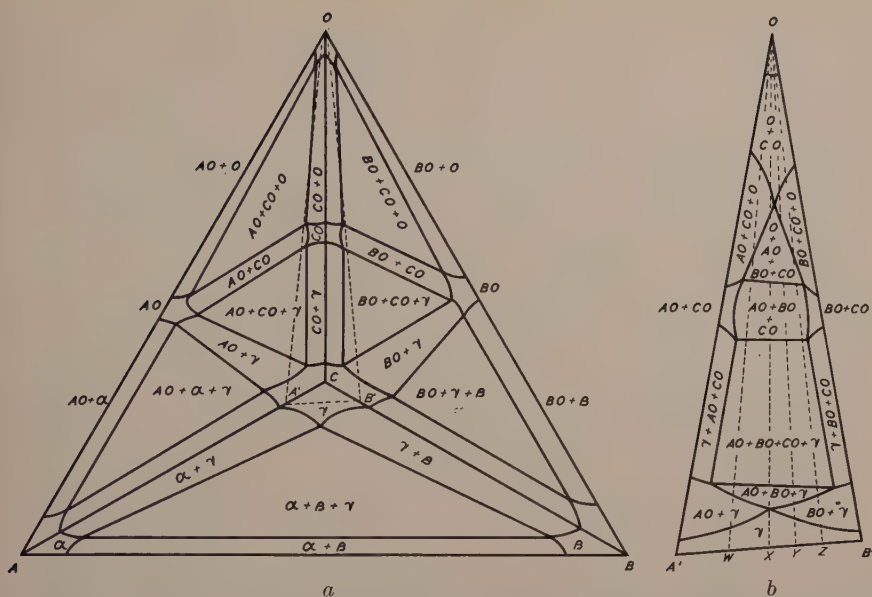


FIG. 32.—SCHEMATIC REPRESENTATION OF CONSTITUTION OF QUATERNARY SYSTEM COMPOSED OF THREE METALS AND OXYGEN.

a is an isotherm and b a section through isotherm taken through region indicated in a by dotted triangle $A'B'O$.

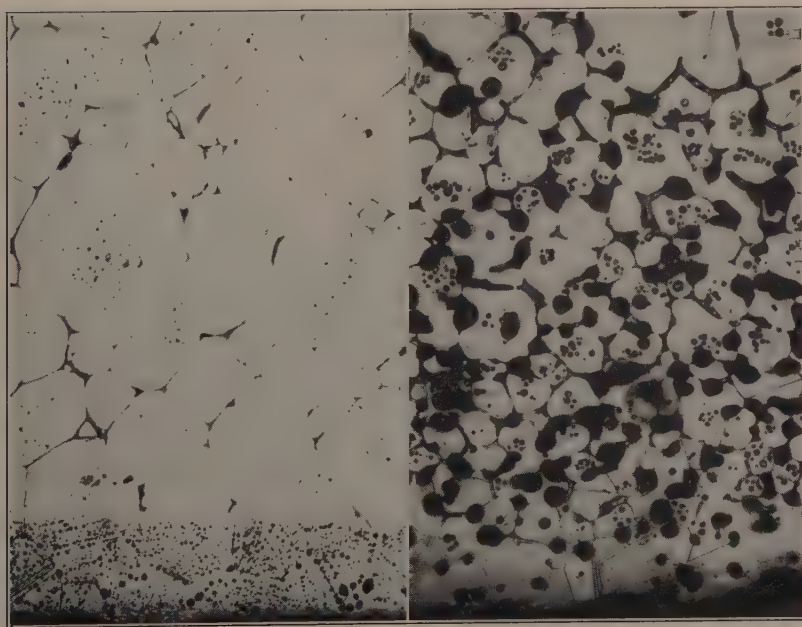


FIG. 33.—ALLOYS OF (a) 0.28 PER CENT CADMIUM AND (b) 2.09 PER CENT PHOSPHORUS OXIDIZED 2 HOURS AT 1000°C. $\times 50$.

32b) along the plane designated by the dotted triangle in Fig. 32a.

Compositions occurring along the side $A'B'$ represent solid solution alloys of C with A + B present in various proportions from A alone to B alone. Such alloys, barring the sensible diffusion of the solute metals in the presence of oxygen, as mentioned in connection with the binary alloys, form a series of scale layers represented by points along the dotted line connecting the alloy with the oxygen corner of the diagram. Thus alloy w forms two subscales, $\gamma + \text{AO}$ and $\gamma + \text{AO} + \text{BO}$ and a surface layer of $\text{AO} + \text{BO} + \text{CO}$ while alloy y reverses the arrangement, forming subscale layers of $\gamma + \text{BO}$ and $\gamma + \text{AO} + \text{BO}$. It is to be anticipated, then, that the identity of the oxide forming the inner subscale can be controlled by a suitable adjustment of the original alloy concentration. At some one concentration only one band will occur, as in alloy x . Cases y and z are related as the alloys of Fig. 31 and 28a, in that the relative widths of the two subscale zones are altered by changing the alloy composition.

In the immediately preceding section it was mentioned that a copper-tin-beryllium alloy was oxidized in a mixture of bronze and stannous oxide. No tin oxide was precipitated, only beryllium oxide. This suggests a method by which the preferential oxidation of certain constituents of an alloy may be accomplished. Obviously there will be no choice of the order of oxidation if the alloy concentration is fixed.

Oxidation Accompanied by Melting

The oxidation of several alloys such as those containing the larger additions of phosphorus or cadmium was accompanied by partial melting when treated at 1000°C. (Fig. 33). Under normal conditions liquation would be expected in these alloys when heated at 1000°C. without oxidation. It might be expected also that the removal of the alloying element from solution in the subscale would eliminate the normal liquation in this zone; something of this sort seems to have occurred in the cadmium alloy Fig. 33a. The rounded outline of the oxide particles suggests, however, that they may themselves have been liquid at the time of formation. In the phosphorus alloy (Fig. 33b), where a much wider subscale has formed, the precipitation is predominantly at the grain boundaries and exhibits clear evidence of having been molten. The similarity between this structure and those of Fig. 18 is striking. Probably the oxygen has again diffused chiefly along the grain boundaries, for it is generally true that diffusion is more rapid in liquids than in solids. Alloys of several other systems that might be expected to exhibit similar liquation showed no evidence of such behavior, possibly because the alloy contents were too low. It has been noted that the external oxidation of the alloys in which melting occurs proceeds at an exceedingly high rate.

Identification of the Oxides

Because of their fine particle size the positive identification of the chemical nature of the precipitates has proved difficult and must form the subject of a separate research. In many cases when only one oxide is known or when the compound has an obviously characteristic color or response to reflected polarized light, it seems altogether reasonable to assume that the precipitate is the oxide so indicated. Thus it is reasonably certain that the oxides Al_2O_3 , SiO_2 and MgO have formed. In other cases, when several oxides are possible, the best hope of identification lies in a determination of the chemical composition or of the crystal structure and parameters of the precipitates. Attempts to obtain X-ray diffraction patterns of the precipitates in place have not yielded promising results. Further experiments designed to separate the precipitates for identification are under way.

SUMMARY

A group of 40 binary copper α -solid solution alloys has been subjected to oxidation at elevated temperatures both in the air and in a closed container packed with a mixture of copper metal powder and cuprous oxide. Internal oxidation has been found in the binary combinations containing Al, Sb, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cb, Ga, Ge, In, Fe, Pb, Li, Mg, Mn, Ni, P, Se, Si, Na, Sr, Ta, Sn, Ti, W, V, Zn, and Zr. External oxidation alone was found in alloys with Ag, Pt and Pd. The behavior of alloys containing Bi, S, Te and Tl was uncertain.

The particle size of the precipitated oxides depends upon the chemical nature of the alloying element, the concentration of the alloy and the temperature of oxidation. Very stable oxides tend to form fine precipitates while the less stable ones form coarse particles. High temperatures of oxidation and high concentrations of the alloying element both favor a large particle size. Extensive agglomeration is rarely found. Occasionally Widmanstätten figures occur.

The distribution of the precipitate varies from system to system and with the temperature of oxidation. In some alloys the particle count increases inward and in others the opposite occurs. A more or less uniform distribution of the oxides, which seems to be characteristic of high-temperature oxidation, gradually changes to precipitation, predominantly at grain boundaries, as the temperature of oxidation is lowered.

The rate of growth of the subscale decreases with time, with an increasing concentration of the alloy, with lower temperatures and with lower oxygen pressures; the time to form a given thickness of subscale is almost directly proportional to the concentration of the alloy; the log of the thickness squared is a linear function of the reciprocal of the absolute temperature.

Ternary alloys containing copper with tin or zinc and aluminum, beryllium, or silicon, all exhibited double zones of internal oxidation, the outer band containing the oxides of both metals and the inner band the oxide of only one metal. The relative widths of the bands can be varied by changing the alloy composition and the precipitation of one of the oxides may be suppressed by sufficiently lowering the oxygen pressure.

Under certain conditions liquation may accompany internal oxidation.

An extensive discussion of the application of phase diagrams to the rationalization of oxidation behavior has been included.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to the staff of the Metals Research Laboratory for assistance and suggestions, and in particular wishes to acknowledge the contributions of Mr. R. Ward and Mr. W. A. Anderson, who carried out the greater part of the experimental work. Special thanks are due also to Dr. C. S. Smith, who rendered assistance in a number of ways.

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DISCUSSION

(R. M. Brick presiding)

E. P. POLUSHKIN,* New York, N. Y.—I should like to ask about the real nature of oxide particles shown in the photographs. Are these particles completely separated

* Consulting Metallurgical Engineer.

from the solid solution, just as the particles of cuprous oxide are in the normal copper-copper oxide eutectic, or are they merely nuclei with some oxide agglomerated around but still remaining within the solution? If the latter is true, how can we know that the particles are really oxides and not something else, since they have not been sufficiently mineralized to exhibit under the microscope a typical color of oxide?

The line of demarcation between the oxidized zone and the normal metal at 1000°C. is straight, whereas in the specimens heated to 600° the oxidation has followed the boundaries and the specific directions within the grains. It seems to me that the explanation of this difference lies in a too violent effect of heat at high temperatures, so that comparatively minute specific differences presented by anisotropy of crystals disappeared entirely. It is desirable that further experiments be carried on at lower temperatures, so that the structural aspects of the process of internal oxidation could be revealed. There is no doubt that the study of all conditions in the subscale has not only scientific interest but also great practical importance. When we observe scale on one grade of copper peeling off easily and in large pieces, while on another grade it stubbornly adheres, we have no explanation for this difference. It is certain that the answer could be found in some specific conditions of internal oxidation, such, for instance, as the formation of films or evolution of gases in the subscale zone.

I feel that we should greatly appreciate Dr. Rhines' valuable contribution to our scant knowledge in this field.

J. L. CHRISTIE,* Bridgeport, Conn.—We hear a good deal about theoretical papers and practical papers. Anyone who has faced the problem of annealing and pickling beryllium copper on the silicon bronzes will find in Dr. Rhines' paper a great deal that is of practical value. While the work was done on a laboratory scale instead of under mill conditions, the understanding of the fundamentals of the problem as brought out in the paper should be a long step forward in the direction of a solution of the practical problem.

A. A. SMITH, JR.† AND J. S. SMART, JR.,† Barber, N. J.—In his description of the experimental procedure the author enumerates four sources of impurity pickup. It seems probable that the impurities already present in the copper and those added with the alloying agents, in most cases, may be regarded as being too low to interfere with the experimental results. However, the impurity pickup from the crucibles and the oxygen content obtained by casting through air may possibly be of much greater influence than is indicated by the blank alloy, No. 82. The writers have observed on numerous occasions that electrolytic copper melted in clay graphite crucibles under reducing conditions increases in impurity content to an appreciable extent. Of the several elements picked up, iron usually represents a large portion of the total, and the amount obtained can be sufficiently high to be of considerable concern in experimental work of the type under consideration.

The criterion as to whether an interfering precipitate of these "blank impurities" was obtained in the present diffusion experiments is, of course, the initial oxygen content of the castings. It is well known that a stream of molten copper poured through air absorbs oxygen rapidly, and that the amount absorbed varies to a large degree between castings in spite of careful efforts to control the conditions. The author's observation that oxide particles were frequently observed in many specimens prepared for test is thus to be expected. The fact that the blank alloy No. 82 showed no precipitation after diffusion can thus be hardly advanced as proof of the absence of interfering impurities, since it is possible that in this sample they were

* Assistant to Vice-president, Handy and Harman.

† Central Laboratory, American Smelting and Refining Co.

already precipitated because of casting conditions that permitted the pickup of the necessary oxygen content.

The melts containing alloying additions are subject to the same interfering factors but the degree of interference is largely dependent on the properties of the added element. The alloys containing appreciable amounts of strong deoxidants having a relatively high solubility, such as phosphorus, silicon and aluminum, are least affected; the impurities picked up in melting are probably present in solid solution, and those that combine with oxygen are then precipitated during the diffusion period along with the alloying element, the latter being present in such excess as to render the interference negligible.

Elements of very low solubility or of high volatility at the temperature of the melt are not only difficult to retain in solution in desirable quantities but are apt to protect the "blank impurities" from oxidation during casting, being further depleted in the process, and possibly existing in the solidified casting in smaller amounts than the "blank impurities." For example, alloy 81, containing only "traces of Ca," shows a rather heavy precipitate for such an analysis, suggesting that the oxides formed may be due to the presence of some other impurity. In this respect, it will be noted that the copper assay of sample 82 is 99.95 per cent, a rather low result for oxygen-free electrolytic copper, which should run about 99.98 per cent (usual limit of accuracy ± 0.01 per cent). Other additions of suspected low solubility, such as tungsten, have not been detected in the samples of analysis and also are open to question. No doubt the author's conclusion that all of the alkaline metals form subscales is correct in view of their high affinity for oxygen but it does not appear that their oxides have been conclusively presented in evidence.

In other instances the results have been described as "uncertain" but the conclusion has been drawn that oxidation takes place; arsenic has been thus described. There are considerable data in the literature to indicate that arsenic can exist in solid solution in copper in the presence of substantial amounts of oxygen, and the low conductivity of oxygen-bearing arsenical coppers is well known. Hanson and Marryat²¹ present evidence that the drop in conductivity is independent of the oxygen content, except for the volume effect of the excess Cu_2O , for a number of arsenical coppers. It would seem that if oxidation of arsenic occurs during diffusion, it would also readily proceed in the presence of an excess of Cu_2O . Again, the identification of the precipitate obtained appears to be of considerable importance.

Inasmuch as the author indicates that the work that has been presented in the present paper will be continued in somewhat more detail, and that identification of the precipitates will constitute a major objective, future results may determine which of the several apparent possibilities in the interpretation of the data are to be preferred. A simultaneous extension of the theoretical treatment already given in the present paper will be of wide general interest and would be a welcome addition to the data already at hand on the phenomenon of diffusion.

F. N. RHINES (author's reply).—The apparent indefiniteness of the boundaries of many of the precipitate particles pointed out by Mr. Polushkin is probably not real, but simply the result of the fineness of the particle size and relief in the polished surfaces. When one of the precipitates, such as SiO_2 , is removed from the copper matrix by dissolving away the metal with acid, it is found to be composed of minute idiomorphic particles, which, upon examination with a petrographic microscope, seem to possess the usual characteristics of the mineral. It is hardly surprising that mere corners of such particles protruding from the opaque copper matrix should fail to show the characteristic colors when it is remembered that the ruby color of

²¹ Hanson and Marryat: *Jnl. Inst. Metals* (1927) **37**, 121-163.

much larger particles of cuprous oxide embedded in copper can be brought out only by the use of polarized or oblique light, and even then with difficulty.

Mr. Polushkin's views with regard to the influence of the temperature range upon the appearance of anisotropy and predominant grain-boundary diffusion are clearly in accord with the observed facts, although it may be questioned whether there is any true parallel between diffusion as such and reaction at surfaces. Further studies at the lower temperatures do, indeed, seem most desirable from a practical standpoint. It should be emphasized, however, that the rate of internal oxidation drops off very rapidly with falling temperature and for practical purposes is probably negligible at a little below 600°C. There is another factor, besides the preferential oxidation along grain boundaries, that may be very important in determining whether or not an oxidized zone may adhere to the base metal—namely, the concentration range of the alloy; peeling of the subscale was almost always observed among the “high”-silicon alloys and not at all among those with “low” silicon.

Mr. Christie's suggestion of a practical application of information on internal oxidation is welcome; to it may be added another that has recently come to the attention of the author. When certain of the internally oxidized alloys are annealed in hydrogen, embrittlement beyond that ordinarily observed in deoxidized coppers that have been annealed in alternately oxidizing and reducing conditions is found. Studies now in progress show that zinc oxide, for example, greatly aggravates hydrogen embrittlement.

Whether or not the quantities of impurities introduced into the alloys by the action of the addition agents upon the crucibles are sufficient to vitiate some of the results of this research, as Messrs. Smith and Smart have suggested, it is altogether appropriate that this factor be given serious consideration. Even though an impurity such as iron is not present to the exclusion of the intended addition, or in an amount sufficient to mask the appearance of the alloy oxide, it may cause the appearance of a second precipitate of iron oxide that would complicate rate studies. The author feels that he has adequate proof that the intended addition agents have been responsible for the effects reported, but is quite willing to concede that iron oxide in minute quantities may be present in any or all of the subscales examined. The experimental proofs are of two kinds: an inductive proof depending upon a crude observation of rates of oxidation and an actual identification of the precipitates formed.

Since the presentation of this paper an additional group of copper-iron alloys has been made and studied and the majority of the alloys in which internal oxidation was found have been analyzed for iron. The largest iron impurity found was 0.035 per cent Fe in the cerium alloy, No. 61. (Commercial cerium, used in making this alloy, carries iron as a principal impurity.) It was found that a binary copper-iron alloy containing 0.0375 per cent Fe will oxidize all the way through in 2 hr. at 1000°C.; i.e., three times as far as the cerium alloy was oxidized. Thus there must be something in the cerium alloy besides iron that is consuming oxygen during internal oxidation. The same argument applies with even greater force to the remainder of the alloy list; the effects observed cannot be accounted for by iron alone, or, since the new iron alloys were made by the former technique, by iron together with the other impurities introduced during melting; they must be due in large part to the intended additions.

Experiments on the direct identification of the oxides are still incomplete, but even at the present stage it is evident that the results will bear out the assertions of the paper in almost all cases. From the 33 alloy systems in which internal oxidation was observed, 20 representative samples have been examined, so far, and the precipitates have been positively identified by X-ray diffraction methods in nine of them as follows: κ - Al_2O_3 , Cr_2O_3 , Fe_3O_4 , Pb_3O_4 , SiO_2 , SnO_2 , TiO_2 , ZnO , and ZrO_2 . More effective methods for isolating the precipitates are being developed for the identifica-

tion of the remainder of the list. Of all of the oxides identified, iron oxide seems to be the most easily detected and all 20 samples have been examined for its presence. Detectable quantities were found only in the copper-iron alloys and in alloy 114 (nominally 0.1 per cent W). As yet the cerium alloy has not been examined, but the list does include calcium, which has been brought into question. The results of this study when completed will be published.

The author feels that the evidence relative to the effect of oxygen upon the conductivity of copper-arsenic alloys is still too confused to argue either for or against the formation of a precipitate of an oxide of arsenic upon internal oxidation. Contradicting the work of Hanson and Marryat is what appears to be an equally careful investigation by Greaves,²² who found that the addition of oxygen to a copper-arsenic alloy materially lowers its conductivity. The consensus seems to be that copper and arsenic form a ternary oxide and it may be this that is precipitating, thus withdrawing a minor quantity of arsenic from solid solution. The zone of internal oxidation was clearly visible in the alloy containing low arsenic, No. 105, but not in No. 62. The behavior in this respect seems to be similar to that of lead.

Finally, it is interesting that the subsequent studies upon the identification of the oxides have shown that the precipitate in alloy 53 (0.1 per cent Fe) is Fe_3O_4 and not FeO or Fe_2O_3 . This oxide appears near the head of Table 2, agreeing with the order of precipitate particle sizes as shown in the photomicrographs of Figs. 6 to 12.

²² Greaves: *Jnl. Inst. Metals* (1912) **7**, 231, 232.

Copper Embrittlement, IV

BY L. L. WYMAN,* MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

THE resultant embrittlement caused by the exposure of oxygen-bearing copper when hot and exposed to reducing gases has been the subject of many studies.¹ Little attention, however, has been given to the possible embrittling effects due to atmospheres or conditions that under some circumstances might be the source of a reducing gas.

At rather infrequent intervals there occur reports of copper becoming embrittled during normal annealing cycles in commercial steam-atmosphered furnaces such as customarily are used for this operation. As might be expected, several other factors exist—such as oil, dirt on the wire, or in the furnace, or metallic surface contacts—that might produce reducing gases and be the source of the trouble. However, in consideration of the statement made by Ruder,² it would seem that under some conditions steam itself might prove to be the source of trouble.

A consideration of the amount of the dissociation of water vapor up to temperatures of the melting point of copper shows that³ the amount of hydrogen that could come from this source is far too minute to account for any embrittlement. What such information does not tell is what will happen at the surface of copper when subjected to steam at elevated temperatures, for entirely different conditions may persist, which would account for Ruder's observation. Furthermore, there are no data as to what might happen at the surfaces of other materials present, the resultant of which might affect the condition of the copper present.

For this reason, it was decided to make a series of experiments comparable to those previously conducted by the writer,¹ which would clarify the effect of the steam on copper, and in copper in the presence of steel.

MATERIAL

The material used in these experiments was tough-pitch copper wire of rectangular cross section, about $\frac{1}{8}$ in. thick, picked at random from the regular factory production of material used for windings, etc., in the electrical industry. Chemical analysis of this material gave the follow-

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* Research Laboratory, General Electric Co., Schenectady, N. Y.

¹ References are at the end of the paper.

ing results: "Spectrographic examination showed the absence of impurities in amounts abnormal for the best grade of electrolytic copper. There were no additions for either hardening or deoxidation . . . examination has shown that the copper is tough pitch of excellent purity." Analysis: copper, 99.968; silver, 0.0009; oxygen, 0.028; sulphur, 0.0007.

METHODS

For the heat-treatment, a Nichrome-wound furnace was constructed. Through this furnace was placed a steel tube connected at one end with a pipe that was attached to the steam line and closed at the other end by a pipe cap, through which a small hole was drilled to permit the escape of steam. At the charging end of the furnace there was also a small pipe tapped into the steel tube, which permitted the drainage of any condensate and also the escape of steam.

The copper samples were cut about $\frac{5}{8}$ in. square, and these samples, after proper stamping for identification, were placed on a "boat" made of a stainless-steel strip in which grooves had been made just wide enough to permit the sample to be stood on edge in the groove. In this way all of each sample, except the very small portion in the groove, could be exposed to the conditions prevailing in the furnace. Inasmuch as the furnace, tube, etc., were large compared to the boat and its contents, the actual time lag due to the introduction of the charge into the furnace maintained at temperature was fairly small.

As already suggested, the furnace was brought up to the desired temperature and the steam valve so adjusted that there was a visible escape of steam, from the small hole in the cap closing the charging end of the furnace tube as well as from the condensate drain pipe. A check on the consumption of water by substituting a drip flask for the steam supply showed that about 75 c.c. per hour was necessary to keep a visible flow of steam from the outlet.

The boat and samples were placed in the center of the length of this furnace, where the heat zone had been determined to be uniform over a length greater than the length of the boat. The furnace was closed immediately and after the pyrometer indicator showed that the furnace and charge had reached the temperature of experiment, samples were withdrawn periodically and immediately quenched in water.

Following this, the samples were sectioned and polished for microscopic examination, to ascertain the depth to which embrittlement, if any, had taken place under the particular conditions of the experiment. Portions of each sample were sharply bent in order to reveal any embrittlement.

In any instance where doubt existed as to the results obtained, repeated runs of additional samples were made for purposes of corroboration.

After very careful metallographic polishing, which ensured the retention of any particles of cuprous oxide that might be left, the samples were examined microscopically in order to determine the dividing line between the part where oxide was still present and the part where it had been removed by reduction, leaving embrittled structure. After the results had been obtained from this examination, the samples were lightly etched with the sulphuric acid, dichromate etching solution and further examined for depth of embrittlement. This method of examination is the same as that used in previous embrittlement work.¹

These experiments were run in 100° steps from 600° to 1000°C., inclusive, with additional steps at 750° and 850°C. added. The time of exposure of the samples to the furnace conditions was in steps of 1, 2, 5,

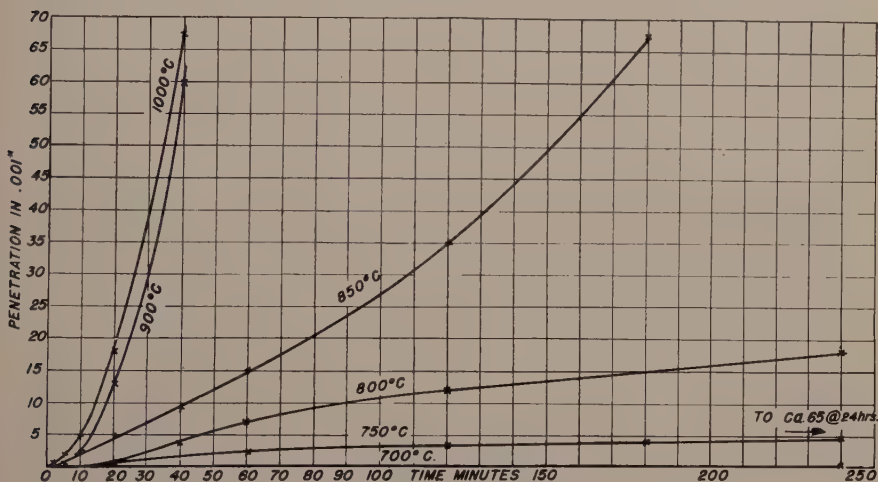


FIG. 1.—RESULTS FROM EXAMINATION OF SAMPLES.

10, 20, 40, 60, 120 and 240 min., in addition to this it was found that after running the 700° test it would be advisable to continue the 750° run and this was carried to 24 hr. at temperature.

Fig. 1 shows the results obtained from the examination of the samples, from which it is evident that there is danger from embrittlement in "steam," but occurring at temperatures that ordinarily are considerably above those normally used in copper annealing.

After being subjected to treatment for 4 hr. at 700°C., the micro-sections of the samples in this group indicated that the oxide particles may have been partly removed in some places, and these samples were conservatively rated as having the maximum of $\frac{1}{2}$ mil embrittlement.

Although the curve at 750° is carried out only as far as 4 hr. in Fig. 1, results of a longer treatment reveal that the curve bent upward somewhat and the sample was nearly completely embrittled at the end of a 24-hr. run. The 800° curve, of course, does show a more intensive attack

on the copper, but it is above 800°C . that the action seems to take place with the greatest rapidity, as witnessed by the large spread in the curves from 800° to 900°C . It is also interesting that there is not a great deal of difference between the 900° and 1000° curves, which might indicate that

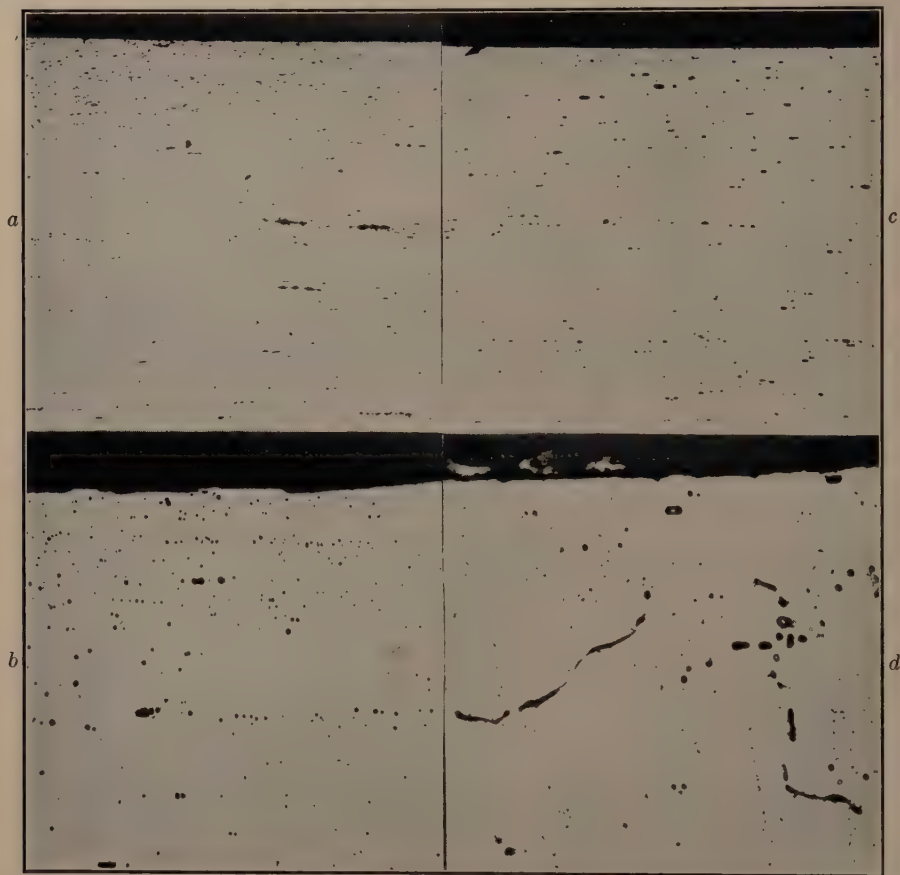


FIG. 2.—OXYGEN-BEARING TOUGH-PITCH COPPER (0.028 PER CENT COPPER). $\times 250$.

- a. As received.
 - b. Heated in steam for 4 hours at 700°C .
 - c. Heated in steam for 4 hours at 800°C .
 - d. Heated in steam for 4 hours at 900°C .
- Lightly etched with sulphuric dichromate.

there is a limiting factor entering into the action and one might legitimately conclude that this may be the amount of hydrogen available.

When the set of curves shown in Fig. 1 was compared to the curves obtained on copper containing very closely the same amount of oxygen, which was run in hydrogen only,¹ it was noted that in both cases the curves grouped together into two sections and that while copper of 0.026 per cent oxygen run in hydrogen shows that the rate of activity

increases markedly above 600°C., the copper used in this experiment (0.028 per cent oxygen) in steam shows this rate to have the marked increase above 800°C.

In the experiments previously cited,¹ it was observed that coincidental with the jump in embrittlement rates there was also an increase in the extent to which the boundaries were "blown open" by the "gas-sing" action.

This holds equally true for the present experiments, as may be judged by comparing photomicrographs of the 800° and 900°C. treatments shown in Fig. 2.

Although the former does not appear to be embrittled, close examination will show that the oxide has been reduced. Furthermore, check tests made by bending the halves of samples not used for microscopic examination corroborated the results of the latter.

Photomicrographs of the copper used in this experiment are shown in Fig. 2 in the as-received as well as in some of the heat-treated conditions.

The foregoing experiments show what might occur in a commercial furnace, containing its nominally designed structure of steel framework and refractories, and its load of copper, in coils and on steel spools. It does not, however, show what will happen with nothing but copper and steam present. Thus, in order to obtain this information, a second series of experiments was conducted.

In order to determine these fundamental values, tests were made in equipment similar to that used in the earlier experiments but in which the enclosing tube was of fused quartz. Into this tube distilled water was trickled at a rate of about 75 c.c. per hr. The flow of steam from the exit end of the tube was comparable in amount to that shown in the first series of experiments. The boat on which the samples were carried was of the same copper as the samples.

The entire schedule described for the first experiments was duplicated, but even after 8 hr. at a temperature of 1000°C. no embrittlement was evident. This is shown in Fig. 3, taken at the very edge of the cross section of the sample that was exposed to the prevailing atmosphere.

It is clearly evident that the presence of unreduced Cu_2O at the very surface of the metal amply denotes the absence of embrittling action

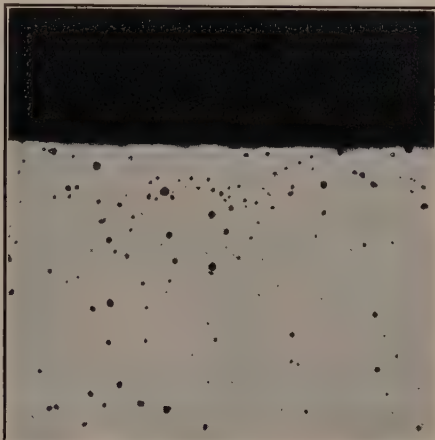


FIG. 3.—HEATED IN STEAM 8 HOURS AT 1000°C. IN QUARTZ.

under circumstances wherein the atmosphere alone is the controlling factor.

CONCLUSIONS

Mention has been made in this paper of the possibility of the greater amount of dissociation of steam due to the presence of metals of various kinds in the furnace, and this is to be interpreted in terms of all the metal present in the furnace, which includes the steel furnace tube and the stainless-steel boat. It has been shown by the second series of experiments that the presence of such metal must affect the results of these experiments, inasmuch as the action at the steel interface causes the formation of the reducing gas (hydrogen) from steam. Inasmuch as the embrittlement produced in this commercial variety of copper under "commercial" annealing conditions could take place only within reasonable lengths of time at temperatures above $700^{\circ}\text{C}.$, it becomes evident that any embrittlement that might be found to have occurred in commercial annealing furnaces using steam atmospheres must certainly, in the light of the second series of experiments, be attributed to causes other than the steam.

It may be logically deduced, therefore, that, inasmuch as steam alone cannot embrittle copper up to periods of 8 hr. at $1000^{\circ}\text{C}.$, and the catalytic action of the presence of iron can produce embrittlement of major importance only at temperatures above $700^{\circ}\text{C}.$, any embrittlement occurring at the customary annealing temperatures must of necessity be due to dirt or grease on the copper; or to such materials as volatile products from the enamel, dirt, grease, lubricants, or other materials carried into the furnace extraneously.

ACKNOWLEDGMENT

The writer wishes to express his gratitude to Mr. C. H. Davis, of the American Brass Co., for making the chemical analyses, and to Mr. H. T. Oatman, who conducted many of the experiments described.

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2. W. E. Ruder: *Trans. Amer. Electrochem. Soc.* (1916) **29**, 515.
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DISCUSSION

(H. M. E. Heinicke presiding)

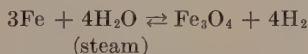
J. C. BRADLEY,* Waterbury, Conn.—When the polished, unetched surface of "gassed" copper is examined, the line of demarcation between the brittle and sound copper can be readily distinguished because the copper and cuprous oxide are of

* Metallurgist, American Brass Co.

different color. After etching, it is frequently difficult to show on a photomicrograph where the cuprous oxide was reduced by hydrogen. In Fig. 2, photomicrographs of four sections of copper, about 0.008 in. thick, are presented. Depth of embrittlement after 4 hr. at 700°C. was found to be 0.0005 in. This would be $\frac{1}{8}$ in. on Fig. 2b. Depth of embrittlement after 4 hr., at 800°C. was found to be 0.018 in., so all of 2c and 2d would show deoxidized copper. I should like to ask the author whether one should be able to see any difference on these photomicrographs between reduced and unchanged copper, or whether the distinction between them has been eliminated in reproduction.

On page 296, "catalytic action of the presence of iron" is mentioned. Is this not a straight chemical reaction between iron and steam, the iron gradually oxidizing and releasing hydrogen? This was experienced with steam inside a cast-steel retort used for annealing copper. The retort was fired on the outside with fuel oil. After nearly two years' use, with temperature at approximately 700°C. at one place, the $1\frac{1}{2}$ -in. steel at this place was oxidized almost clear through from both sides and was very brittle, save for a $\frac{1}{16}$ -in. unoxidized shell in the middle.

R. H. COWEN,* Washington, D. C.—The action of steam on certain metals and the resulting embrittlement has occupied the attention of several investigators in recent years. It is in the light of their results that the conclusions that you have drawn as to the cause of the embrittlement of copper are of interest, especially the conclusions regarding the catalytic action of iron. The presence of steel as the conductor for steam to the stainless-steel "boat" is not "catalytic" in action, but it takes an active part as it is an excellent source for the generation of hydrogen at the temperatures used in the tests. This action is based on the reaction:



which is used commercially for the generation of hydrogen. The work done by C. H. Fellows, of the Detroit Edison Co., during 1927 and by R. M. Van Duzer, of the same company, from 1934 to 1937 proved conclusively that steel pipe subjected to high-temperature steam generates appreciable quantities of hydrogen. The results of these investigations have been confirmed by A. A. Potter and H. L. Solberg at Purdue University. The latter investigators found that steam at 1100°F. (593°C.) will even attack 18-8 and 25-20 stainless steel. The rate of this reaction is appreciable at about 900°F. (482°C.) and increases with temperature. It seems obvious that even if the copper is freed of "extraneous" materials, the presence of steel and high-temperature steam will exert its destructive action of embrittlement. The additional fact that the rate of diffusion of hydrogen through copper increases markedly with temperature offers a fertile field for the attack of hydrogen in the copper oxides present, with the resulting reduction and embrittlement.

C. S. SMITH,† Waterbury, Conn.—It should be pointed out that hydrogen can be formed from steam not only by reaction with iron but with almost any other reducing material, whether metallic or carbonaceous. In addition to excluding iron from furnace charges, it is also necessary to avoid the presence of traces of oil and organic matter in order to prevent embrittlement of copper by the production of hydrogen. As Mr. Wyman emphasizes, embrittlement from this source does not occur to a serious extent except above about 550°C., although hydrogen would have caused considerable damage at this temperature.

* Naval Research Laboratory, Anacostia Station.

† Research Metallurgist, American Brass Co.

By way of confirmation of the author's findings I should like to give the results of some mechanical tests on copper heated in steam, with and without iron. Samples of NEC copper wire of 0.080-in. diameter, containing 0.036 per cent oxygen, were heated in a silica tube in an atmosphere of steam produced from distilled water in a

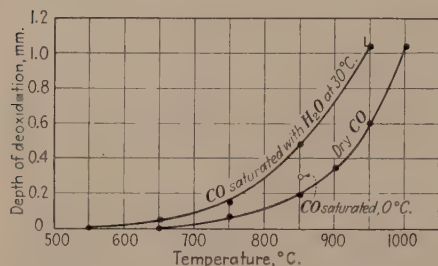


FIG. 4.—DEPTH OF DEOXIDATION OF COPPER WIRE ON HEATING IN DRY AND IN WATER-SATURATED CARBON MONOXIDE.

deoxidation in the sample heated alone, while the wire heated in the presence of iron in steam had been completely deoxidized to its center, with intergranular cracking.

Statements are to be found repeatedly in the literature to the effect that carbon monoxide embrittles copper. Some experiments were run to check this.* Carbon monoxide was generated by dropping CP formic acid into concentrated sulphuric acid at 100°C. and freed from water vapor and carbon dioxide by passing successively through sulphuric acid, barium perchlorate (Desicchlora) and sodium hydroxide (Ascarite). The dried gas then passed through a silica tube, containing the copper-wire specimens, which was placed in a hot furnace and rapidly heated to the desired temperature. The pressure was substantially atmospheric. Bend tests were made on the treated wires and the depth of penetration was measured microscopically. Pieces of 0.40-in. diameter rod containing 0.037 per cent oxygen were included on many runs. The data obtained are summarized in Figs. 4 to 7 and some tensile data are given in Table 1. Although heating in dry carbon monoxide has little effect on the number of bends the wires will withstand, deoxidation has occurred to a considerable depth. On the other hand, carbon monoxide saturated with water at 30°C. (vapor pressure of water at 30°C. is 31.8 mm. Hg) severely embrittles the wire. Much less but still appreciable embrittlement occurs if the carbon monoxide contains water up to the saturation limit at 0°C. (vapor pressure of water at 0°C. is 4.6 mm. Hg).

Heating in dry carbon monoxide for 30 min. at temperatures below 950°C. leaves a core of copper containing the original amount of oxide visible under the microscope. On subsequent heating in hydrogen for 30 min. at 850°C., wires in this condition become internally brittle and develop surface blisters. The part of the wire from

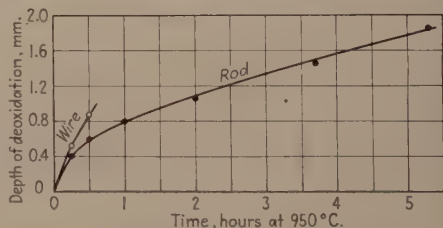


FIG. 5.—DEOXIDATION OF COPPER WITH DRY CARBON MONOXIDE AT 950°C.

* Since this discussion was written a masterly paper by Ransley has appeared [*Jnl. Inst. Metals* (1939) **65**, 147-171] confirming the deoxidation of copper by carbon monoxide without embrittlement and showing a remarkably high rate of diffusion of oxygen.

which the oxide has been removed by carbon monoxide treatment remained ductile after a subsequent hydrogen anneal.

TABLE 1.—*Tensile Properties of Copper Wire Heated in Reducing Atmospheres^a*

No.	Atmosphere	Temperature of Treatment, Deg. C.	Tensile Strength, Lb. per Sq. In.	Elongation on 2 In., Per Cent	Bends (r = 0.2 In.)
11	Steam.....	850	33,600	39.2	14-14-10-13
12	Steam + iron.....	850	21,200	11.2	½-½-1-½
1	Dry CO.....	850	35,100	36.5	13-15-13-12
2	Dry CO (2 hr.).....	850	35,500	35.8	13-13-13-12
4	CO saturated with H ₂ O at 0°C.	850	35,200	33.3	4-6-7-8
10		850	32,850	39.0	8-9-10-9
6	Carbon monoxide saturated with water vapor at 30°C.	550	34,750	45	13-13-12-11
7		650	33,400	39.8	8-9-8-7
5		750	32,000	23.8	4-4-4-3
3		850	23,000	11.5	1-1-½-1
9		850	22,200	13.5	1-½-½-½-½
8		950	29,000	18.3	1-1-2-1

^a Wire 0.08-in. diameter containing 0.036 per cent oxygen, 0.0022 per cent sulphur. All treatments for 30 min. at temperature except where otherwise stated. Tensile properties average of two tests. Individual bend test results given. See Figs. 4 to 7 for additional bend tests after other treatments.

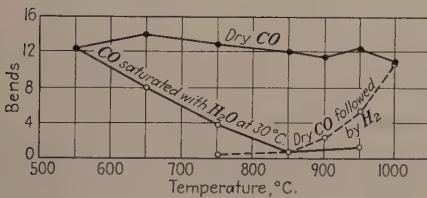


FIG. 6.

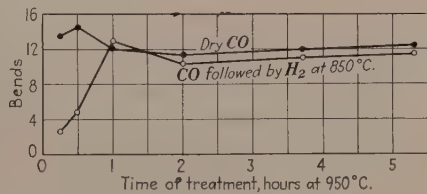


FIG. 7.

FIG. 6.—EFFECT OF HEATING IN CARBON MONOXIDE ON DUCTILITY OF COPPER.

Number of bends to fracture is number of 180° reverse bend cycles over radius 2.5 times diameter of wire.

FIG. 7.—BEND TESTS ON COPPER HEATED IN DRY CARBON MONOXIDE AT 950°C. AND ON SAME WIRE AFTER SUBSEQUENT HEATING IN HYDROGEN FOR 30 MINUTES AT 850°C.

L. L. WYMAN (author's reply).—The necessity of selecting a magnification that will conveniently show the total depth of embrittlement and at the same time be sufficient to show the presence or absence of cuprous oxide in the spots creates a dilemma which is not at all improved by reproduction; thus all of the photomicrographs in Fig. 2 cannot hope to show the depth of embrittlement in its initial stages.

As to the action of steam with iron, the statement in the paper is correct with respect to the copper. Also, in corroboration of the example given by Mr. Bradley, I found that the 3-in. iron pipe used in the first part of these experiments had been completely oxidized after 300-hr. use at the experimental temperatures.

Even though hydrogen can be produced by the reaction of steam with ferrous materials at temperatures of 500°C. or so (as cited in the discussion) the amount of H_2 produced must be considered insignificant in so far as the present subject matter is concerned. This is verified by the fact that at 600°C. no embrittlement was evidenced after 24 hr. under conditions wherein the amount of exposed iron was very great in comparison to the amount of copper present. At higher temperatures, however, even a few iron spools carrying copper may well prove to be sources of troublesome embrittlement by the extraneous presence of the iron.

Dr. Smith's discussion of the effects of wet and dry carbon monoxide, as well as his citation of Ransley's work, go far to clarify the embrittlement problem.

Summing up the present knowledge of this entire situation, it would seem that hydrogen is the offender, regardless of how it happens to be formed and present; and, given enough of it, embrittlement may occur even at 500°C.

Practically speaking, this resolves itself into several "rate" problems that are subject to time, temperature, hydrogen production, etc., which establish conditions below which oxygen-bearing copper must be annealed in order to eliminate the embrittlement hazard.

Simultaneous Diffusion of Nickel and Silicon in Solid Copper

BY ROBERT F. MEHL* AND FREDERICK N. RHINES,† MEMBERS A.I.M.E.

(New York Meeting, February 1939)

RELATIVELY few data have been collected on the rates of diffusion in ternary solid solution systems. In general it does not seem worth while to gather extensive data for such systems until the factors that determine the rates of diffusion in binary systems are better understood. But the rates of diffusion in a ternary system of limited solid solubility, in which the terminal solid solution is in equilibrium with an intermediate phase and may thus be represented as a quasibinary system, represents a case of special interest. In this case, where by reason of the association of the two solute metals in an intermediate phase a special attraction of the two solute atoms may be safely assumed, some interaction of these atoms during simultaneous diffusion in the solvent lattice might be expected.

It has frequently been proposed that molecular solid solutions exist in quasibinary and in other ternary (and binary) solid solutions. There is no direct evidence for such solid solutions; arguments based upon the supposed anomaly in certain physical properties¹ are hardly important; unexpected density relationships have proved deceptive;² suggestions of molecular solid solutions have been made on the basis of solution laws in their application to certain systems, but without result;³ attempts to find lattice parameters in the solid solution Al-MgZn₂, which cannot be calculated from the separate effects of magnesium and zinc and might therefore be taken as evidence for a molecular aggregation, have given negative results.⁴

Fundamentally, methods for the determination of the state of molecular aggregation in solution depend upon the kinetic behavior of the particles constituting the system. If it could be shown that the two solutes in a quasibinary ternary system diffuse in molecular proportions, despite a radical difference in the separate rates of diffusion of each solute when diffusing alone in the solvent lattice, some basis for the concept of molecular solid solution would be afforded. Freche⁵ examined the rates of

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independent and simultaneous diffusion of magnesium and silicon in aluminum—the quasibinary system $\text{Al-Mg}_2\text{Si}$ —and concluded from her measurements that magnesium and silicon tend to diffuse in the molecular proportions of Mg_2Si when the alloy core contains magnesium and silicon in this ratio.

The system $\text{Cu-Ni}_2\text{Si}$ is especially well adapted to the study of the possibility of molecular diffusion. The individual rates of diffusion of nickel and of silicon in the terminal copper solid solution are known, and these rates differ markedly; the variation in these rates with both solute concentration and temperature are sufficiently well known. Grube and Jedelev⁶ determined the diffusion coefficient D for the system copper-nickel

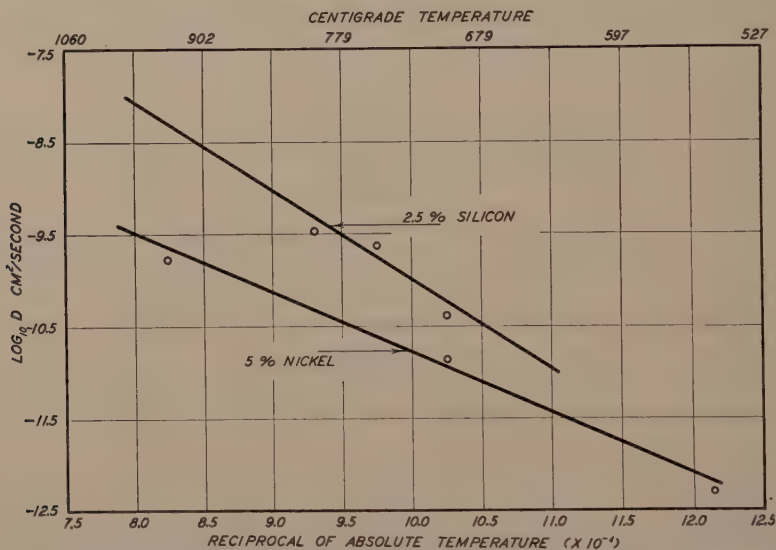


FIG. 1.—PLOT OF VARIATION OF DIFFUSION COEFFICIENT WITH TEMPERATURE FOR 5 PER CENT NICKEL IN COPPER AND FOR 2.5 PER CENT SILICON IN COPPER, EACH DIFFUSING ALONE.

at 1025° C.; Matano⁷ recalculated these data so that D could be expressed as a function of concentration and also determined the coefficient for diffusion between an alloy of copper and nickel with 10 atomic per cent Ni and pure copper, for the temperatures 550°, 700°, 950° C. Since the method employed in this latter work did not permit the calculation of D as a function of concentration, his results may be taken as pertaining to the average composition, 5 atomic per cent; Matano's data are plotted in Fig. 1. Rhines and Mehl⁸ determined the rate of diffusion of silicon in copper over a temperature and a concentration range (0.5 to 7.0 atomic per cent Si, 700° to 800° C.); the relationship between D and temperature is plotted in Fig. 1, extrapolated to 1000° C.; the curve refers to a concentration of 2.5 atomic per cent Si, just half the concentration of nickel, 5 per cent, shown in the figure. The relationships plotted in Fig. 1 may

be regarded as representing the rates of diffusion of nickel and silicon in copper in an alloy with 7 to 8 mole per cent Ni_2Si on the assumption that each rate is independent of the other; i.e., that there is no interaction. It may be seen that the rate of diffusion of silicon is much greater than that of nickel; if the curves are extrapolated to lower temperatures, they cross at a temperature in the neighborhood of 500°C ., at which the two rates are identical. At such a temperature nickel and silicon would diffuse from a core alloy containing nickel and silicon in the stoichiometric proportions of Ni_2Si , and maintain the stoichiometric proportions of Ni_2Si during diffusion, assuming no solute interaction, but at no other temperature would this quasimolecular diffusion appear. If, despite the great difference in the separate D values for nickel and silicon, these two solutes should diffuse in molecular proportions over the whole observed temperature range, this behavior might be taken as evidence for molecular diffusion.

Crepaz⁹ reports that Ni_2Si forms a quasibinary system with copper; the solid solubility of Ni_2Si in copper is given as 2.5 weight per cent at 500°C ., slightly less than 5 weight per cent at 880°C ., and about 10 weight per cent at 1100°C . In order to confirm the conclusion of Crepaz that this is in fact a quasibinary system, the nature of the precipitate from the terminal solid solution has been shown below by means of X-ray diffraction identification to be Ni_2Si .

This paper, accordingly, will present data on the rates of simultaneous diffusion of nickel and silicon from a solid solution alloy of copper and Ni_2Si into pure copper, and will attempt to interpret them particularly with respect to solute atom interaction.

EXPERIMENTAL

Identification of Precipitate in System Cu- Ni_2Si .—Although Crepaz studied the etching characteristics of Ni_2Si in a cast alloy in which the secondary phase was known to be Ni_2Si , in the present work no etching test was found that could be used to conclusively identify the precipitated phase, and it was necessary to resort to X-ray diffraction identification. An unusually heavy precipitate was induced at the surface of a sample with 4 weight per cent Ni_2Si by the technique developed by Brick and Phillips,¹⁰ consisting in polishing the surface of a freshly quenched sample, followed by aging; the homogenization was made at 1000°C . for 16 hr., and the aging was performed at 450°C . for 116 hr. For comparison, pure Ni_2Si was made by melting nickel and silicon together in the proper proportions, with the final composition verified by chemical analysis. The powder diffraction lines for Ni_2Si and for the precipitated alloy were obtained in a Weisenberg camera with a gas tube furnishing pure copper radiation.

Table 1 lists the diffraction lines obtained from the precipitated alloy, together with the comparison lines for copper and for Ni_2Si . The Ni_2Si

lines from the precipitate all occur at an angle about one degree smaller than those from the pure Ni_2Si comparison sample; owing, no doubt, to a saturation of the Ni_2Si precipitate with copper and a consequent slight change in lattice parameter and reflection angles. Three β reflections of copper and four Ni_2Si lines are missing in the pattern from the precipitated alloy, but these are all weak lines. The excellence of the agreement leaves little doubt that the precipitate in this binary system is in fact Ni_2Si .

TABLE 1.—*X-ray Diffraction Data*

θ Observed	Intensity Observed	θ for Cu	Index of Cu Reflections	θ for Ni_2Si	Intensity of Ni_2Si Lines
72.0	Strong	72.0	α 024		
		70.0	β 224		
68.2	Very strong	68.2	α 133		
		59.0	β 024		
58.3	Weak	58.6	α 004		
57.3	Very weak	56.8	β 133		
		50.3	β 004	49.1	Very weak
47.6	Strong	47.6	α 222		
46.9	Extremely weak			45.9	Medium
45.0	Very strong	45.0	α 113		
44.0	Extremely weak			43.6	Weak
43.1	Extremely weak			42.3	Weak
41.7	Very weak	41.7	β 222		
39.6	Weak	39.6	β 113		
38.6	Extremely weak			37.8	Very weak
37.0	Strong	37.0	α 022		
36.1	Very weak			34.9	Very weak
33.2	Very weak	32.9	β 022		
28.4	Extremely weak			26.8	Weak
25.1	Medium	25.3	α 002	24.6	Medium
				23.9	Very weak
24.5	Very weak			23.0	Strong
22.7	Very weak	22.6	β 002		
				22.3	Weak
21.7	Very strong	21.7	α 111	21.7	Weak
19.4	Medium	19.5	β 111	20.4	Very weak

Determination of Rates of Diffusion.—The experimental technique and the methods for the analysis of data used here have been completely described elsewhere;⁸ it need only be said here that two core alloys were employed, one containing approximately 4 weight per cent Ni_2Si and the other approximately 8 weight per cent Ni_2Si ; these were received in the form of rolled rods about $\frac{3}{4}$ in. in diameter. Each bar was machined accurately to a cylindrical shape and electroplated with copper to a thickness of 2 mm. Each plated bar was given a diffusion anneal for the time period listed in Table 2; layers of about 0.003 in. were then

machined from the bar and analyzed. The analytical data are recorded in Table 3.

TABLE 2.—*Diffusion Conditions*

Sample No.	Core Analyses (Balance Copper)		Temperature of Diffusion, Deg. C.	Time of Diffusion, Days
	Weight Per Cent Nickel	Weight Per Cent Silicon		
1	6.54	1.57	1000 \pm 1	0.97
2	3.20	0.81	850 \pm 1	51.55
3	3.18	0.80	850 \pm 1	53.65

TABLE 3.—*Diffusion Data*

Sample No.	Distance from Interface, Mm.	Weight Per Cent Nickel	Weight Per Cent Silicon	Sample No.	Distance from Interface, Mm.	Weight Per Cent Nickel	Weight Per Cent Silicon
1	0.645	0	0.02	3	0.846		0.02
1	0.419	0	0.05	3	0.784	0	
1	0.257	0.10	0.08	3	0.595		0.07
1	0.145	0.56	0.26	3	0.530	0	
1	0.097	1.05	0.36	3	0.396		0.12
1	0.048	1.66	0.40	3	0.340	0.17	
1	-0.006	3.10	0.68	3	0.268		0.17
1	-0.061	4.60	1.10	3	0.198	0.51	
1	-0.163	5.94	1.46	3	0.135	0.94	
1	-0.312	6.50	1.53	3	0.074	1.53	0.38
1	-0.544	6.52	1.60	3	0.009	1.53	0.46
				3	-0.065	1.89	
2	0.665		0.04	3	-0.119	2.29	0.62
2	0.488	0.20	0.04	3	-0.241	2.71	0.73
2	0.273	0.35	0.14	3	-0.392		0.79
2	0.128	0.94	0.27	3	-0.465	3.25	0.82
2	0.081	1.20		3	-0.532		0.78
2	0.027	1.95	0.29	3	-0.739	3.18	0.80
2	-0.022	1.81	0.36	3	-0.797		0.83
2	-0.076	1.94	0.38				
2	-0.123	2.16	0.48				
2	-0.181		0.521				
2	-0.224	2.59					
2	-0.285		0.61				
2	-0.408	3.03					
2	-0.705	3.20					
2	-0.755		0.81				

THE DATA

Microscopic study of samples of the 8 per cent Ni_2Si alloy annealed at 1000° C. and quenched showed the presence of a very small quantity of

Ni_2Si not in solution; similar inspection of the 4 per cent Ni_2Si alloy annealed at 800°C . and quenched showed a like small quantity of undissolved Ni_2Si ; evidently the values given by Crepaz for the solubility of Ni_2Si are somewhat higher than the true values. The selection of the solution to Fick's law for application to diffusion-penetration curves depends upon whether the core alloy, on the one hand, is a homogeneous solid solution, or, on the other hand, contains undissolved solute to an extent that will maintain the solubility concentration of the solute at the

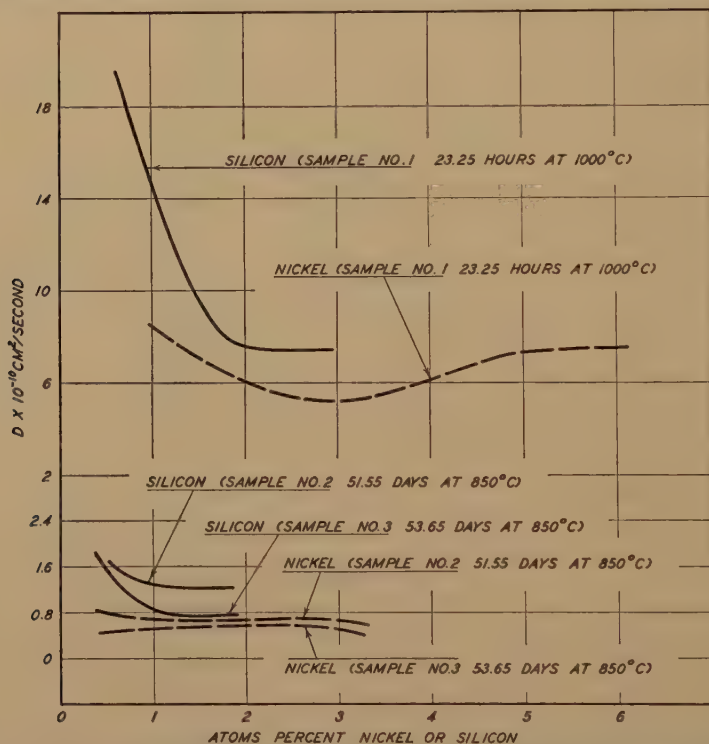


FIG. 2.—PLOT OF VARIATION OF DIFFUSION COEFFICIENT WITH CONCENTRATION FOR NICKEL AND SILICON DIFFUSING TOGETHER FROM A COPPER SOLID SOLUTION OF Ni_2Si INTO PURE COPPER.

interface throughout the diffusion anneal.¹¹ The presence of only a slight amount of undissolved Ni_2Si in the bar treated as described suggests that the present case is an intermediate one; the diffusion-penetration curves plotted from the data given in Table 3 are, however, of the symmetrical type characteristic of diffusion of a solute from a solution without excess solute into a pure solvent (ref. 11, eg. 5), rather than from a saturated solution containing excess solute as a separate phase into a pure solvent (ref. 11, eq. 4). In view of this, it is possible that the D values quoted below are slightly lower than the true values, but the difference can hardly be more than a few per cent of the order of accuracy of the measurements.

The D values calculated from the data given in Table 3, employing the solution of Fick's law for diffusion from a solution without excess solute into a pure solvent, as developed by Matano⁸ are plotted in Fig. 2.

DISCUSSION OF RESULTS

The D values for nickel and silicon diffusing separately into copper and the D values for nickel and silicon diffusing simultaneously into copper are listed in Table 4. These values are so selected as to facilitate a comparison of separate and simultaneous diffusion at identical concentrations of each solute, with the two solute concentrations in the stoichiometric ratio of Ni_2Si . These comparisons could be made on other bases, but the one given will suffice for the purpose.

TABLE 4.—*Comparison of Diffusion Coefficients*
(D in Sq. Cm. per Sec. $\times 10^{-10}$)

Temperature, Deg. C.	Composition, Per Cent	Nickel		Silicon	
		Alone	With Silicon	Alone	With Nickel
1000	1 Si, 2 Ni	10	6	71	14
	2 Si, 4 Ni	6	6	98	8
	3 Si, 6 Ni	5	7	150	8
850	1 Si, 2 Ni	2	0.7	13	1
	1.5 Si, 3 Ni	1.5	0.7	23	1

It will be seen that the D values for nickel are relatively little affected at either temperature by the presence of silicon. The D values for silicon, however, are greatly decreased by the presence of simultaneously diffusing nickel, to less than one-tenth at higher silicon contents. Since diffusion occurred from a core alloy containing nickel and silicon in the stoichiometric ratio of Ni_2Si , an equivalence of the D values for simultaneous diffusion could be taken as evidence of molecular diffusion. The D values for nickel and silicon diffusing simultaneously are not appreciably different in the higher concentrations at 1000°C ., as shown in both Table 4 and Fig. 2, but appear to differ markedly at lower concentrations.

A better test may be obtained by comparing the ratio of the atomic percentages of nickel and silicon in the individual sample cuts for analysis, taken from Table 3. Table 5 shows these ratios, and shows also the atomic percentages from which the ratios were derived and the sample cuts to which the ratios refer. The values at the bottom of the table are those near the core, and the values at the top of the table are those near the limit of penetration of nickel and silicon into the copper plate; i.e., the ratios at the bottom of the table are for high nickel and silicon solute concentrations and those at the top for low nickel and silicon solute concentrations. The atomic ratios of nickel and silicon in the two core alloys

were chosen to be equal to two for Ni_2Si and are near this value. At greater distances from the core—i.e., at lower and lower concentrations of nickel and silicon—the atomic ratio in all samples becomes less and less, departing from the stoichiometric ratio of two for Ni_2Si to an increasing degree. Thus, with increasingly dilute solutions the rate of diffusion of silicon becomes increasingly greater than that of nickel. This is shown also in Fig. 3, in which the effect of temperature on the D values at lower concentrations is illustrated. It must be concluded, therefore, that nickel and silicon do not simultaneously diffuse into copper in the stoichiometric proportions of Ni_2Si , though tending to approach this condition to an increasing degree as the concentrations increase.

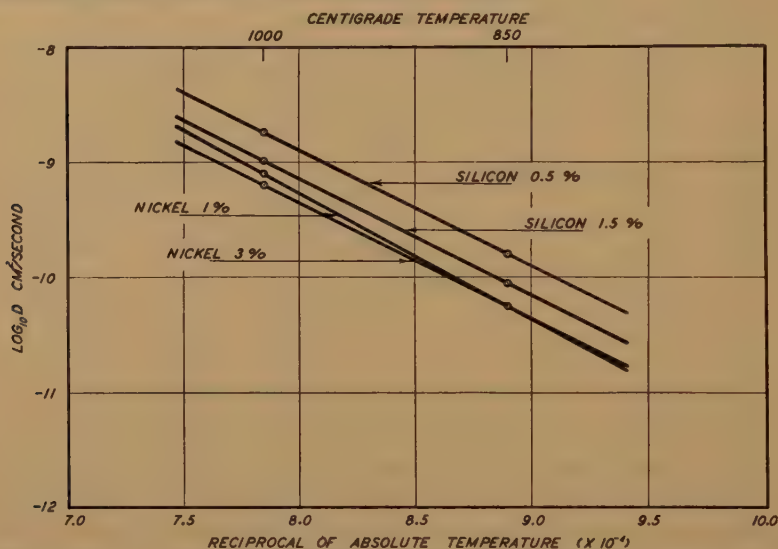


FIG. 3.—PLOT OF VARIATION OF DIFFUSION COEFFICIENT WITH TEMPERATURE FOR 1 ATOM PER CENT NICKEL AND 0.5 ATOM PER CENT SILICON DIFFUSING TOGETHER AND FOR 3 ATOMS PER CENT NICKEL AND 1.5 ATOMS PER CENT SILICON DIFFUSING TOGETHER.

It is a highly interesting and important fact that the interaction of nickel and silicon in diffusing simultaneously in copper is such as to approach the ratio of Ni_2Si : the rapidly diffusing silicon is retarded by the more slowly diffusing nickel, whereas the slowly diffusing nickel is little if any affected. It might be assumed on this basis that molecular diffusion occurs, but that the molecules at each stage of dilution dissociate to a fixed degree, with the degree of dissociation increasing with dilution in an orthodox fashion, Table 5.

The concept of molecular diffusion and therefore of molecular solid solutions is, however, not a very attractive one, for it is difficult to visualize a molecule—a tri-atomic molecule in the present case—moving through the lattice of the solvent. On the basis of cyclic interchange of atoms¹¹ the probability of a sufficient number of cyclic atom interchanges of the

right sort to make room for the molecule would certainly be small; on the more modern theory of Wagner-Schottky,¹² which assumes vacant lattice positions and the occupation of interstitial positions by atoms, it seems highly unlikely that a molecule, necessarily large, could occupy an interstitial position, or that a sufficient number of adjacent vacant lattice positions should be available in the path of the diffusing molecule with sufficient frequency to provide the observed mobility of nickel and silicon, particularly since the mobility of nickel is essentially unchanged in the presence of silicon, which would imply that the molecule moves as rapidly as the nickel atom. An assumption of molecular diffusion, however, is not required to explain the present data.

TABLE 5.—*Nickel-silicon Ratio*

Distance of Sample Cut from Original Interface, Mm.	Ratio of Atoms, Per Cent of Nickel to Silicon								
	Sample 1, Atoms Per Cent			Sample 2, Atoms Per Cent			Sample 3, Atoms Per Cent		
	Si	Ni	Ratio	Si	Ni	Ratio	Si	Ni	Ratio
+0.3				0.26	0.40	1.54	0.42	0.28	0.67
+0.2	0.35	0.25	0.715	0.39	0.70	1.79	0.56	0.64	1.14
+0.1	0.75	1.0	1.33	0.55	1.16	2.11	0.78	1.18	1.52
+0.05	1.10	1.78	1.62	0.64	1.43	2.24	0.92	1.47	1.60
0	1.52	3.30	2.17	0.74	1.70	2.30	1.07	1.76	1.64
-0.05	2.25	4.68	2.18	0.85	1.96	2.31	1.22	2.04	1.67
-0.1	2.84	5.58	2.00	0.97	2.20	2.29	1.36	2.31	1.70
-0.15	3.15	6.15	1.95	1.10	2.47	2.24	1.48	2.55	1.72
-0.2				1.21	2.70	2.23	1.57	2.76	1.76
-0.3				1.41	3.05	2.16	1.70	3.10	1.82

The average time of sojourn of an atom on a lattice point is inversely proportional to the diffusion coefficient, as van Liempt has pointed out.* As a silicon atom moves in the lattice of the ternary solid solution with no immediately neighboring nickel atoms, the time of sojourn of the silicon atom on each lattice point is approximately that for silicon moving in a lattice of the binary copper-silicon solid solution. When, however, the silicon atom becomes adjacent to a nickel atom, the stronger nickel-silicon bonds tend to retain the silicon atom on its lattice point for a longer time, and thus tend to retard the rate of movement of the silicon atom, to decrease the rate of diffusion of silicon. Since the time of sojourn of a nickel atom on a lattice point is greater than that of a silicon atom, any bond between adjacent nickel and silicon atoms tending to increase the

* Van Liempt has given formulas¹³ by which the time of sojourn of an atom on a lattice point may be calculated. It does not seem possible to apply such formulas in a quantitative way to the present case, and the argument is accordingly left merely in a qualitative form.

normal times of sojourn of both atoms would have a greater effect upon the atom whose time of sojourn is normally the lesser, particularly if the increase in the time of sojourn is not greatly in excess of the time of sojourn of the more slowly moving atom. Such a mechanism accounts for a decrease in the rate of diffusion of silicon and for an essentially unaffected or only slightly affected rate of diffusion of nickel. On this basis the effect should be most marked in the more highly concentrated solution, the incidence of nickel and silicon atoms on adjacent lattice points would be more frequent and the delay in the movement of the atoms accordingly more frequent; while in more dilute solutions the incidence of nickel and silicon atoms on adjacent lattice points is correspondingly less frequent and the delay in the movement of the silicon atoms also less frequent. Such a bond between nickel and silicon atoms is doubtless of a chemical type, of the sort operating in the intermediate phase Ni_2Si .

Other data support this view. Bungardt and Bollenrath¹⁴ have studied the rate of diffusion of magnesium in aluminum and in an alloy of aluminum with 2.7 per cent Zn. At 510°C , D for magnesium diffusing in aluminum is 38.4×10^{-10} sq. cm. per sec., and D for magnesium diffusing in the alloy of aluminum with 2.7 per cent Zn is 15.05×10^{-10} sq. cm. per sec. The rate of diffusion of zinc in aluminum at 510°C . is approximately 21×10^{-10} sq. cm. per sec.* Thus in the quasibinary system Al-MgZn_2 , in the simultaneous diffusion of magnesium and zinc, the rate of diffusion of the more rapidly diffusing solute, magnesium, is lowered, and the rate of diffusion of the more slowly diffusing solute, zinc, is but little affected: the data are not sufficiently accurate to permit a more precise statement. Freche's data⁵ on the simultaneous diffusion of magnesium and silicon in aluminum may be used in a similar way; the rate of diffusion of magnesium when diffusing alone at 510°C . is (extrapolated) in the neighborhood of 1000×10^{-10} sq. cm. per sec., while that of silicon is 15×10^{-10} sq. cm. per sec.; for simultaneous diffusion, the rate of diffusion of magnesium from an alloy with 0.644 per cent Mg_2Si is 50×10^{-10} sq. cm. per sec. and from an alloy with 0.644 per cent Mg_2Si and 0.66 per cent Si 10×10^{-10} sq. cm. per sec., while the rate of diffusion of silicon from the first alloy is about 15×10^{-10} sq. cm. per sec. and from the second alloy about 10×10^{-10} sq. cm. per sec. The data of Brick and Phillips¹⁵ for the rate of diffusion of magnesium when diffusing alone give (extrapolated) 80×10^{-10} sq. cm. per sec.; unpublished data from this laboratory give 50×10^{-10} sq. cm. per sec.; Bungardt and Bollenrath¹⁴ give 35×10^{-10} sq. cm. per sec. Although the data on magnesium alone differ widely, all of the data show that magnesium diffuses more rapidly than silicon, and that during simultaneous diffusion the rate of diffusion of the more rapidly

* Unpublished research, Metals Research Laboratory; the value given has been extrapolated from values calculated from diffusion data obtained for lower temperatures.

diffusing magnesium is greatly decreased and the rate of diffusion of the more slowly diffusing silicon is but little affected. Here again the data are not sufficiently accurate to permit a more precise statement.

SUMMARY

1. The rates of diffusion of nickel and silicon when diffusing simultaneously into copper have been determined at 1000° C. and 850° C. and compared to the rates of diffusion of nickel and silicon when diffusing separately into copper.

2. The ternary system involves the quasibinary system Cu-Ni₂Si; the solid solubility of Ni₂Si in copper decreases with decreasing temperature. The precipitate has been found by X-ray diffraction identification to be Ni₂Si.

3. The rate of diffusion of the rapidly diffusing silicon is markedly decreased by the presence of nickel, whereas the rate of diffusion of the slowly diffusing nickel is little if any affected by the presence of silicon. It is shown that the quasibinary systems Al-MgZn₂ and Al-Mg₂Si exhibit a similar behavior.

4. This pronounced interaction of nickel and silicon during simultaneous diffusion is the more marked the higher the concentration. Since equality in the diffusion coefficients of nickel and silicon when these solutes diffuse from a core alloy containing nickel and silicon in the proportions of Ni₂Si is equivalent to the diffusion of molecules of Ni₂Si; the data thus appear to show an approach to molecular diffusion at high concentrations and an increasing departure from this at low concentrations, as though increasing dissociation were occurring on dilution.

5. Molecular diffusion is quite unlikely. The data can best be explained by the occurrence of momentary strong bonds between nickel and silicon atoms when these atoms are on adjacent lattice positions, with a resultant retardation in the rate of movement of the more rapidly diffusing solute silicon.

ACKNOWLEDGMENT

The authors wish to acknowledge their indebtedness to Mr. H. P. George and Mr. Raymond Ward for their assistance in carrying out this research. The alloys were kindly supplied by the American Brass Company.

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DISCUSSION

(R. M. Brick presiding)

D. W. SMITH,* New Kensington, Pa.—At what temperature was precipitation of Ni_2Si for identification made to take place? In some other quasibinary systems—e.g., $\text{Al-Mg}_2\text{Si}$ and Al-MgZn_2 —there is evidence to indicate that at low aging temperatures the precipitating phases may be greatly removed from the equilibrium compositions or crystal structures.

If the precipitation in the alloys studied by Mehl and Rhines was made to take place at a somewhat lower temperature, would they also find nonequilibrium precipitate compositions and structures? If such were the case, one might expect relative diffusion characteristics of the nickel and silicon different from those noted by these authors where the compound Ni_2Si is known to precipitate.

F. N. RHINES (author's reply).—The precipitates identified as Ni_2Si were made by furnace cooling from 1000°C ., whereby it appears probable that if there should be a high-temperature and a low-temperature form of the precipitate this would be the former. The suggestion that the relative rates of diffusion of nickel and silicon might change abruptly at some temperature, owing to the greater stability of some other compound at lower temperatures, is very interesting. The experimental examination of such a case would be made difficult, however, by the very slow rates of diffusion obtaining at the low temperatures.

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Constitution and Microstructure of Copper-rich Silicon-copper Alloys

BY CYRIL STANLEY SMITH,* MEMBER A.I.M.E.

(Chicago Meeting, October, 1939)

SOMEWHAT over ten years ago the author described studies^{1,2} on the constitution of the copper-silicon system. The copper-rich portion of this diagram is shown in Fig. 1. The experimental points freely dotted about the diagram seemed to justify an otherwise unconvincing diagram and for several years the curious reverse bend in the alpha-phase boundary was accepted as substantially correct, even by later investigators^{3,4} of the system who introduced changes in the high-silicon phases. The binary diagram has been used as a base for several ternary systems⁵⁻⁹ without any suggested changes. Voce¹⁰ suspected the existence of another phase from his study of the cast alloys in the copper-manganese-silicon system, but evidently hesitated to extrapolate this to the binary diagram, particularly in view of the too ingenious explanation that was advanced¹¹ to account for the pools of constituent clearly visible in castings; namely, that they were secondary alpha of twinned orientation deposited from beta.

Von Schwarz,¹² in 1932, called attention to the fact that this micro-constituent in copper-silicon alloy castings was anisotropic under polarized light and asserted that a new phase, not cubic, should be placed in the diagram adjacent to alpha. Sautner,¹³ on the basis of investigations with the polarizing microscope and with X-rays, introduced this phase into the diagram at about 6 per cent Si. The relevant part of his diagram is shown in Fig. 2. Sautner called the new phase beta, renaming the old beta phase zeta. To avoid confusion, in redrawing Fig. 2 the phases have been renamed in accordance with the terminology adopted in the present paper, in which the new phase is called kappa and the other phases retain the designation given them by Arrhenius and Westgren.⁴

The thermodynamic impossibility of Sautner's diagram and the paucity of experimental data left the exact location of the new phase field most uncertain, although his work proved beyond doubt that an additional noncubic phase exists. Because of the industrial importance

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¹ References are at the end of the paper.

constructed the diagram shown, with the phases renamed, in Fig. 3. Okamoto also described the curious microstructures observed in the two-phase region, which Corson¹⁶ had previously noticed but had dismissed as due to the precipitation of gamma. Isawa found the new phase to be hexagonal close-packed in structure, $a = 2.553 \text{ \AA}$, $c/a = 1.626$. He believed it to be stable at all temperatures below 830°C . Okamoto reproduces previously unpublished photomicrographs taken by Imai, which show that after long annealing at 400°C . kappa partially decomposes to a eutectoid of alpha plus gamma.

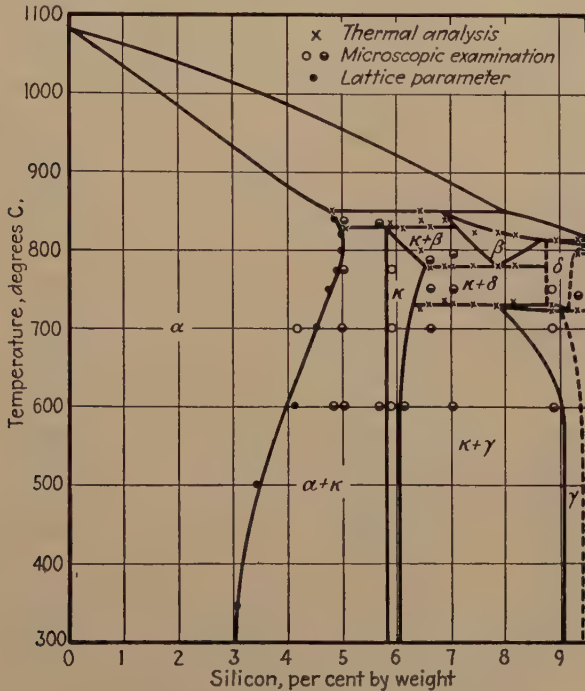


FIG. 3.—DIAGRAM ACCORDING TO ISAWA (1938).

PREPARATION OF ALLOYS

The alloys for the present investigation were prepared from cathode copper and silicon crushed and purified by the acid washing treatment suggested by Tucker.¹⁷ Silicon treated in this way retained 0.26 per cent Fe, but the copper-silicon alloys made from this contained about 0.04 per cent Fe, some having been absorbed from the Acheson graphite crucibles used. No significant amounts of other impurities were found. To facilitate the "wetting" and solution of the finely divided silicon before it oxidized, it was mixed with one-tenth of its weight of sodium fluoride and poured in a slow stream on to the surface of the copper at a

temperature of about 1150°C. The silicon dissolved almost instantly with a loss of only 0.05 to 0.12 per cent, in spite of its finely divided form. A few castings were made from a master alloy containing 21 per cent Si.

The alloys for thermal analysis were cast in a small crucible in which was mounted a core to make a hole for the thermocouple. Those intended for microscopic studies were poured into lampblack-dressed cast-iron molds, $\frac{5}{8}$ in. square, making ingots weighing 300 grams. Segregation almost always occurred in the castings, sometimes giving a center of sufficiently different composition to be observed in the microstructure on a cross section. This core was ignored in reporting the structures.

TABLE 1.—*Composition of Alloys Used for Annealing Experiments*

First Series		Second Series		1928 Alloys	
Alloy No.	Silicon, Per Cent	Alloy No.	Silicon, Per Cent	Alloy No.	Silicon, Per Cent
3338	2.03	3451	3.65	10	4.14
3339	3.98	3452	3.77	11	4.48
3340	4.59	3453	4.03	76	3.83
3341	4.95	3454	4.17	78	3.50
3342	4.92	3455	4.42		
3343	5.22	3456	4.60		
3344	5.40	3457	4.70		
3345	5.54	3458	4.91		
3346	5.92	3459	5.12		
3347	6.08	3460	5.39		
3348	6.28	3461	5.74		
3349	6.60				
3350	6.80				
3351	6.99				
3352	6.99				

All samples were analyzed in duplicate.* Copper was determined by electrolysis, using stationary cathodes, and the silicon was determined gravimetrically. The total of silicon plus iron plus copper was not infrequently as high as 100.04 per cent. Since the silicon determination was regarded as the more precise, it was taken as the true composition of the alloy.

The compositions of all the alloys used for the microscopic examination are listed in Table 1. A few alloys from the 1928 work were used to fill in the gaps for the low-temperature anneals.

* The chemical analyses were performed under the general direction of Ralph P. Nevers, by E. M. Horton, whose competent work it is a pleasure to acknowledge.

THERMAL ANALYSIS

The diagram resulting from the present investigation was principally established on the basis of the microstructures of quenched samples, but the temperatures of the various invariant reactions were determined by thermal analysis when reaction was fast enough. The technique was essentially that described in the author's earlier papers,² but a silica tube was used in preference to the graphite sheath to protect the chromel-alumel thermocouple from a reducing atmosphere. When solid reactions alone were involved no sheath was used, but the couple was placed bare in a cored hole in a cast lump of the alloy.

The peritectic reaction $\alpha + \text{liq.} \rightleftharpoons \beta$ occurred at 851° on cooling and 852° C. on heating in alloys containing both 5.59 and 6.37 per cent Si. An alloy with 5.93 per cent Si gave an arrest on heating at 853° C. These temperatures are in agreement with the old figure of 852° C.

On the cooling curves made in 1928 on alloys containing between 5 and 7 per cent Si there appeared a weak arrest at temperatures between 811° and 832° C. but this was masked because of the greatly increased rate of cooling following the long peritectic arrest. No heating curves were taken and the arrest was erroneously ascribed to the formation of α from β along the strongly sloping line as then drawn. It is now obvious that it is due to the $\alpha + \beta \rightleftharpoons \kappa$ reaction.

New cooling curves were taken at a slow rate by heating gradually until the peritectic reaction just started and then immediately decreasing the furnace current for cooling. Under these conditions large and unmistakable arrests were found at temperatures as shown in Table 2. There seems little doubt that the temperature for the reaction should be placed at about 842° C.

The temperatures of the β eutectoid decomposition and δ peritectoid formation now have been placed at 785° and 729°, respectively,

TABLE 2.—*Thermal Arrests*

Alloy No.	Silicon, Per Cent	Rate of Heating or Cooling, Deg. C. per Min.	Temperature of Arrest, Deg. C.	
			Heating	Cooling
3394	5.59	3.4	846	
		5.0		838
3395	6.37	3.8	844	
		5.0		837
3484	5.93	2.7	845	
		5.0		841
		3.3	845	
		4.8		841

TABLE 3.—*Summary of Heating and Cooling Curves*

Alloy No.	Silicon, Per Cent	Rate of Heating or Cooling, Deg. C. per Min.	Temperature of Beta Decomposition, Deg. C.		Temperature of Delta Formation, Deg. C.	
			Heating	Cooling	Heating	Cooling
3517	7.89	3.7, 4.3		783		724
		5.6, 2.6	785		736	
		2.1, 3.0		783		723
3518	7.4	4.2, 3.1	786		737	
		2.8, 2.6		785		722
		4.6, 3.0	786		737	
		2.4, 2.8		785		721
Averages....			786	784	737	722

as a result of the heating and cooling curves summarized in Table 3. These temperatures are in excellent agreement with those given by Iokibe (783° and 730° C.), and are slightly higher than those reported in the author's earlier papers (782° and 726° C.).

The decomposition of kappa takes place so extremely slowly that it can not be determined by thermal analysis. The determination of this temperature by annealing experiments will be described later in this paper.

ANNEALING AND QUENCHING EXPERIMENTS

The alloys were worked whenever possible in order to break up the cast structure and accelerate diffusion. The castings were annealed 15 hr. at 750° C. then heated to 825° C., and when possible hot-rolled to 0.25 in. thick, then given a homogenizing anneal for 21 hr. at 750° C. (series 3338 to 3352) or 17 hr. at 800° C. (series 3451 to 3461) followed by quenching. The alloys containing up to 5.2 per cent Si hot-rolled perfectly, those from 5.4 to 5.7 per cent rolled with some cracks, but from 5.8 to 6.8 per cent Si the bars cracked so badly that they had to be recast and utilized without working, although they were given the same homogenizing and subsequent treatments.

The first series of alloys (3338 to 3352) was used after hot-rolling and homogenizing and the second series (3451 to 3461) was cold-rolled 50 per cent prior to the final annealing treatments, as these alloys were intended for studies of reactions at lower temperatures.

Samples sawed from the appropriate strips after homogenizing and sometimes cold-working as above were annealed for periods of time ranging from a few hours at the highest temperatures to three months at 400° C., and then quenched and the microstructures examined. A full list of all annealing temperatures and times is given in Table 4. Annealing was performed in tube furnaces equipped with automatic control, the

TABLE 4.—*Annealing Temperatures and Times*^a

Temperature of Annealing, Deg., C.	Duration of Annealing, Hr.	Temperature of Annealing, Deg. C.	Duration of Annealing, Hr.
870	2	645	71
855	7½	594	112
845	3	573	262
835	7	561	195
826 ^b	18½	554	192
815	7	549	168
793	5	543	410
769	26	494	669
743	228	443	400
719	47	394	2,215 ^c
694	17		

^a All samples were given a homogenizing anneal and quench prior to the annealing treatment stated above. Alloys 3451 to 3461, 10, 76 and 78 were cold-rolled 50 per cent before reheating.

^b Annealed 2 hr. at 845° C., slowly cooled to 826° C. and held 18½ hr. at 826° C.

^c Specimens quenched after 672 hr. at 394° C. and when possible given further 50 per cent reduction by cold-rolling prior to replacing in furnace for completion of anneal.

temperature being checked at suitable intervals with a calibrated chromel-alumel thermocouple and a portable potentiometer. The fluctuation due to the control rarely amounted to more than $\pm 2^\circ$ C. and the true temperatures do not differ from the nominal by more than this. The samples were held in a Nichrome tray and were not protected in any way from oxidation. Oxidation was never very great, and the oxidized surface layer was removed completely before the structures were examined.

ETCHING

The unfortunate failure of the author to notice the kappa phase in 1928 was a result, *inter alia*, of the use of a bichromate etching reagent that gives a clean etch, minimizing the difference between alpha and kappa. The ordinary ammonia and hydrogen peroxide etch works fairly well but it can be improved by the addition of potassium hydroxide to dissolve the silica film. This gives a clean etch on alpha and lightly stains the kappa phase. The following composition was used: hydrogen peroxide (30 vol.), 20 parts by volume; water, 25; 20 per cent potassium hydroxide solution, 5; ammonium hydroxide (0.90 sp. gr.), 50. The peroxide should be added not more than an hour before use. The reagent is used at room temperature. Etching time varies between 2 and 30 sec., depending on the effect desired. On specimens containing partly decomposed beta it was found advisable to give a light swabbing with the bichromate reagent before applying the peroxide etch.

THE DIAGRAM

The microstructures observed on the various samples after annealing are summarized in the constitution diagram, Fig. 4. The exact composition and annealing temperatures for the points plotted can be found in Tables 1 and 4. As discussed below, some of the alloys in the alpha plus gamma field still retained undecomposed kappa. There is no doubt that

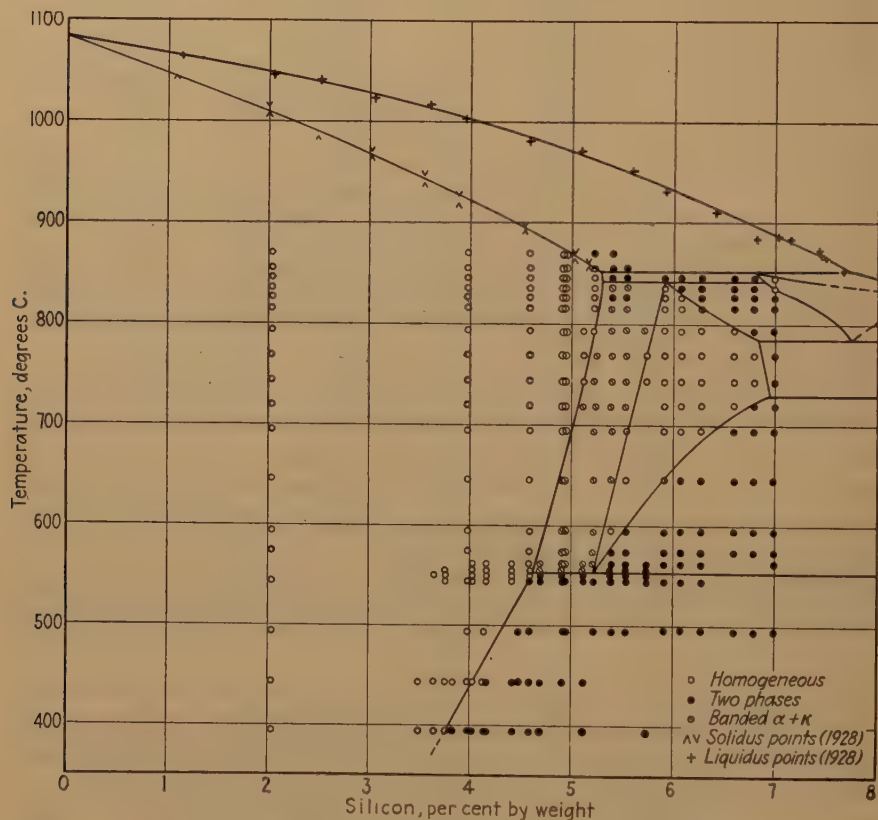


FIG. 4.—NEW DIAGRAM SHOWING EXPERIMENTAL POINTS.

alpha plus gamma is the equilibrium structure. The diagram without experimental points is shown in Fig. 5. The liquidus and solidus points are taken from the 1928 work, since there seems to be no reason to doubt their accuracy, but the rest of the diagram is based on the new work described in this paper.

In Fig. 5 the temperatures and concentrations of the various fixed points on the diagrams are marked and need little discussion. The concentrations of the various phases at the fixed points are given below Fig. 5, in both atomic and weight percentages. The composition limits

of beta, kappa and delta are taken principally from the 1928 work. Almost every one of the newly determined points falls (within the experimental error of about 0.1 atomic per cent) at one of the simple ratios

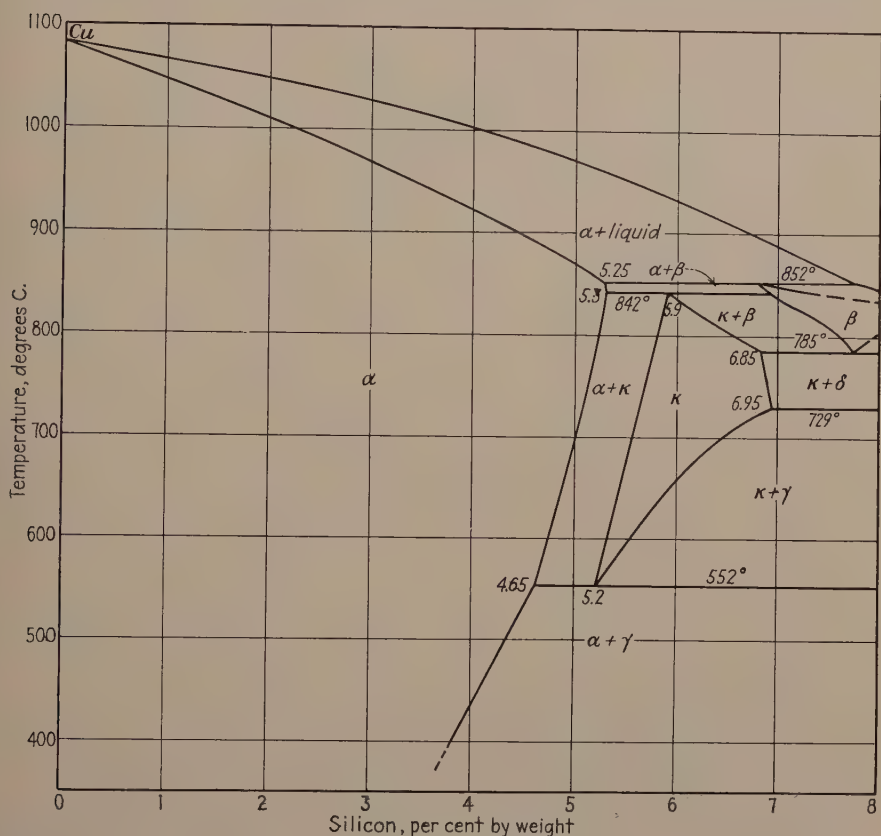
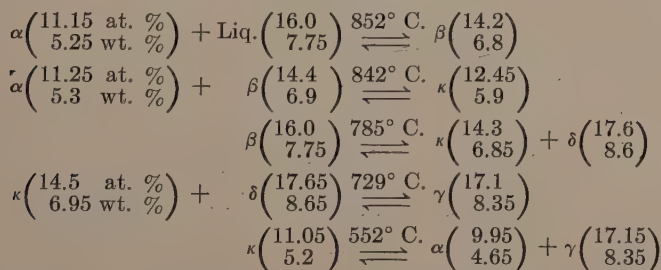
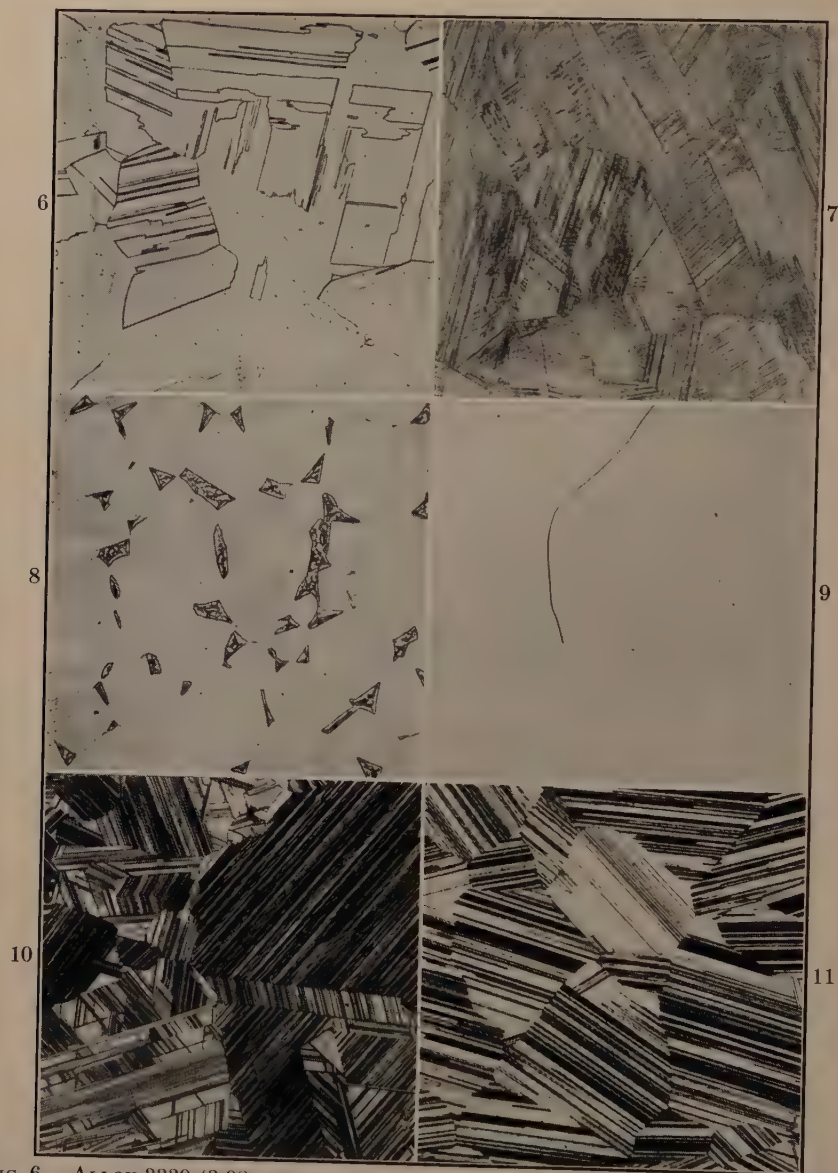


FIG. 5.—CONSTITUTION OF COPPER-SILICON ALLOYS UP TO 8 PER CENT SILICON.

Concentrations of Phases at Fixed Points



of one atom of silicon to 6, 7, 8 or 9 of copper; i.e. 14.29, 12.50, 11.11, or 10.00 atomic per cent Si.



- FIG. 6.—ALLOY 3339 (3.98 PER CENT SI). QUENCHED AFTER 41 HOURS AT 743° C. α .
 FIG. 7.—ALLOY 3343 (5.22 PER CENT SI). QUENCHED AFTER 18.5 HOURS AT 826° C. α .
 FIG. 8.—ALLOY 3344 (5.40 PER CENT SI). QUENCHED AFTER 3 HOURS AT 845° C. $\alpha + \text{decomposed } \beta$.
 FIG. 9.—ALLOY 3346 (5.92 PER CENT SI). QUENCHED AFTER 41 HOURS AT 743° C. κ .
 FIG. 10.—ALLOY 3342 (4.92 PER CENT SI). QUENCHED AFTER 262 HOURS AT 573° C. $\alpha + \kappa$.
 FIG. 11.—ALLOY 3343 (5.22 PER CENT SI). QUENCHED AFTER 41 HOURS AT 743° C. $\alpha + \kappa$.

All $\times 100$. Alkaline peroxide etch except for Fig. 8, for which the etch was potassium bichromate.

MICROSTRUCTURAL CHARACTERISTICS OF THE PHASES

Alpha has the usual twinned polygonal structure associated with the primary solid solutions of copper (Fig. 6). As the silicon increases, the number of twin bands in the annealed structure increases, and near the limit of solubility the grains develop extensive markings that probably result from quenching or polishing strains (Fig. 7).

The beta phase is difficult to retain on quenching and usually shows a duplex structure, particularly when supersaturated with copper in relation to its eutectoid composition (Fig. 8).

The identification of kappa by etching is not easy. The best identification of kappa seems to be that it etches clearly without any twin bands (Fig. 9). It is attacked rather less readily than alpha but is slightly stained by the peroxide reagent described. The kappa phase is weakly anisotropic in polarized light and it could be identified by this property were it not for the fact that the banded duplex alpha + kappa structure gives much brighter polarization effects by virtue of its superficial arrangement. Even silicon-rich alpha shows slight anisotropy.

When kappa exists in equilibrium with alpha in worked and annealed samples it is in bands which at first sight appear to be twin markings (Figs. 10 to 13). Since alpha itself becomes heavily twinned when rich in silicon, it is sometimes difficult to decide whether the markings are kappa or twins in the alpha. However, the rate of etching is much greater in the duplex fields and a little experience with etching the structures permits a positive identification.

By way of convincing skeptics that this banded structure really corresponds to an equilibrium two-phase region in the diagram and is not a transition structure, specimens were annealed in the alpha + beta range for 2 hr., furnace-cooled to 826° C. and held 18½ hr. at this temperature. Since the beta had already collected into areas distinct from alpha (Fig. 8), the kappa resulting from it by reaction was of necessity formed in the same place and a typical two-phase structure resulted instead of the bands. This is clearly shown in Figs. 14 and 15. In castings that have not been worked, the kappa phase is largely segregated in the last parts of the dendrite to solidify and is clearly outlined. Had castings been used instead of wrought alloys in 1928 the kappa phase would probably have been discovered then.

The temperature of the $\text{kappa} \rightleftharpoons \text{alpha} + \text{gamma}$ reaction was established by annealing experiments. Samples cold-rolled 50 per cent after quenching from 800° C. almost all became alpha + gamma on reannealing for a week at 549° C. (Fig. 16), though in some samples a little residual kappa remained. Annealing at 554° C. for eight days always left the kappa phase entirely undecomposed (Fig. 17). The eutectoid transformation is therefore between 549° and 554° C. and has tentatively been placed

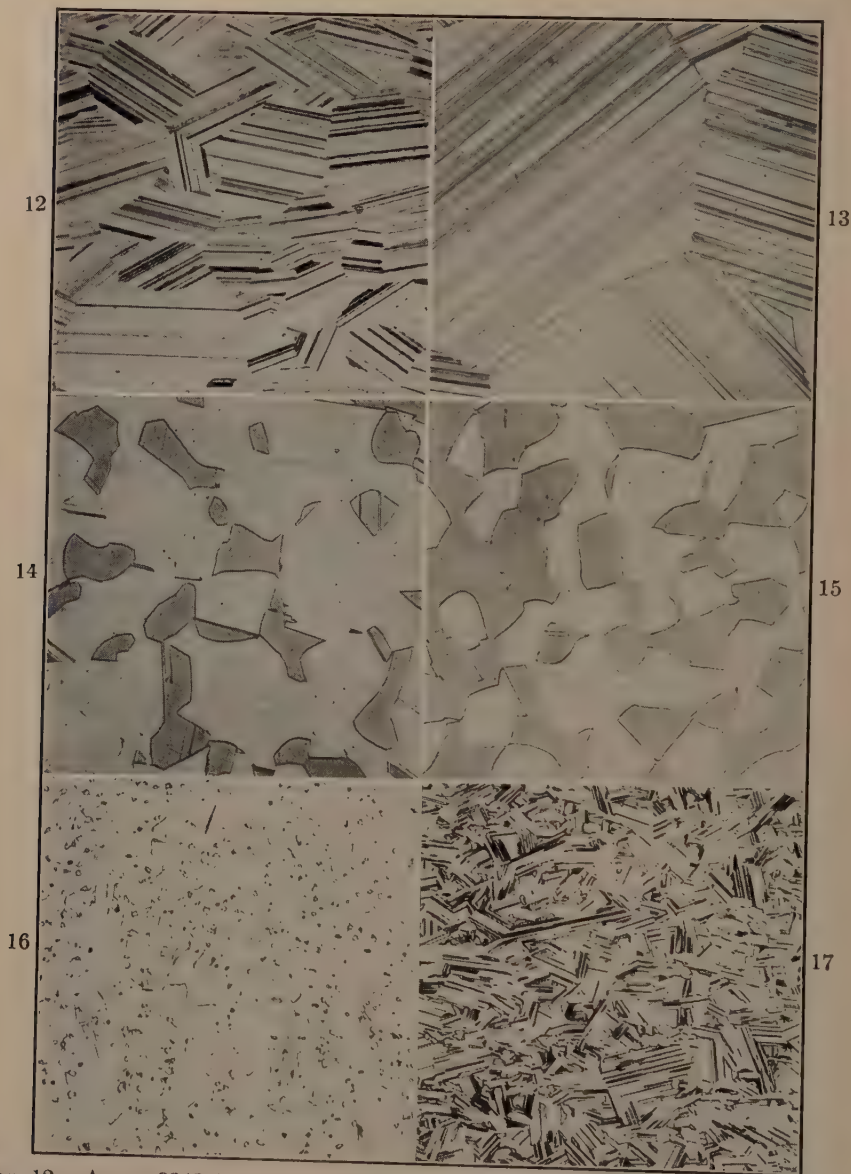


FIG. 12.—ALLOY 3343 (5.22 PER CENT SI). QUENCHED AFTER 262 HOURS AT 573° C. $\alpha + \kappa$.

FIG. 13.—ALLOY 3345 (5.54 PER CENT SI). QUENCHED AFTER 5 HOURS AT 793° C. $\alpha + \kappa$.

FIG. 14.—ALLOY 3344 (5.40 PER CENT SI). ANNEALED 2 HOURS AT 845° C., SLOWLY COOLED TO 826° C. AND QUENCHED AFTER 18.5 HOURS AT 826° C. $\alpha + \kappa$.

FIG. 15.—ALLOY 3345 (5.54 PER CENT SI). SAME TREATMENT AS FIG. 14. $\alpha + \kappa$.

FIG. 16.—ALLOY 3457 (4.70 PER CENT SI). COLD-ROLLED 50 PER CENT AFTER HOMOGENIZING ANNEAL, THEN REANNEALED 168 HOURS AT 549° C. AND QUENCHED. $\alpha + \gamma$.

FIG. 17.—ALLOY 3459 (5.12 PER CENT SI). COLD-ROLLED 50 PER CENT AFTER HOMOGENIZING ANNEAL AND REANNEALED 192 HOURS AT 554° C. $\alpha + \kappa$.

All $\times 100$ except Fig. 13, which is $\times 500$. Alkaline peroxide etch.

at 552° C. As a further check, samples that had been previously annealed at 443° C. to become alpha + gamma were reannealed at 561° C. when they reverted to the equilibrium structure with banded kappa.

Samples quenched from 750° C. and not cold-worked suffered the eutectoid transformation very slowly. Fig. 18 shows the structure of a sample containing 4.59 per cent Si quenched from 750° C. and directly

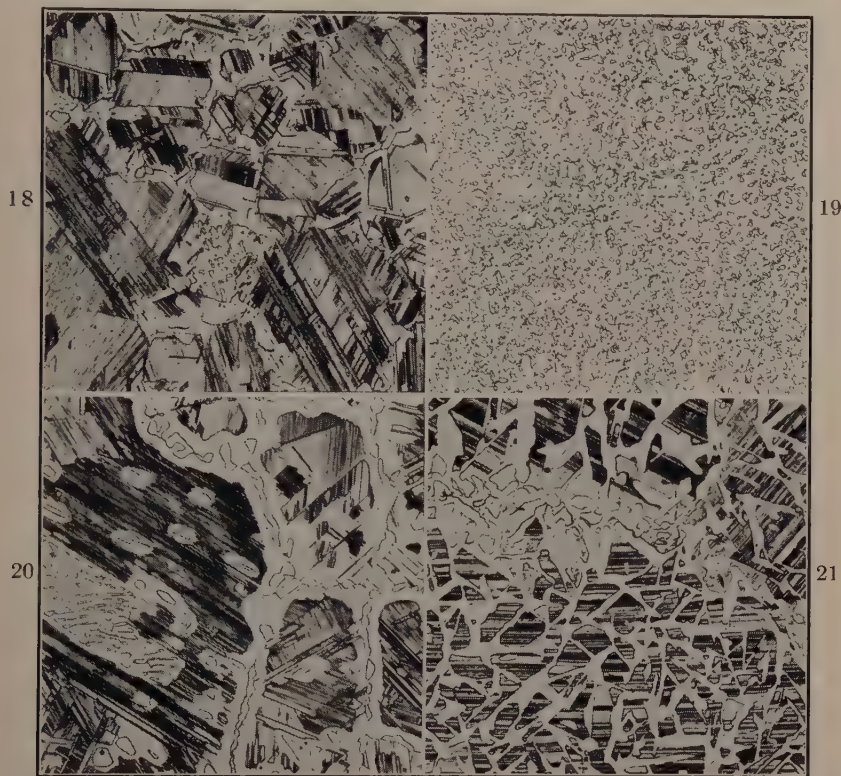


FIG. 18.—ALLOY 3340 (4.59 PER CENT Si). ANNEALED 400 HOURS AT 443° C. NOT COLD-WORKED AFTER HOMOGENIZING ANNEAL. PARTLY DECOMPOSED $\alpha + \kappa$.

FIG. 19.—ALLOY 3340 (4.59 PER CENT Si). PORTION OF SAME SPECIMEN AS FIG. 18, SQUEEZED TO 20 PER CENT REDUCTION BEFORE ANNEALING. $\alpha + \gamma$.

FIG. 20.—ALLOY 3342 (4.92 PER CENT Si). ANNEALED 669 HOURS AT 494° C. $\alpha + \kappa$, PARTLY DECOMPOSED TO γ .

FIG. 21.—ALLOY 3346 (5.92 PER CENT Si). QUENCHED AFTER 669 HOURS AT 494° C. $\gamma + \alpha +$ PARTLY DECOMPOSED κ .

All $\times 100$. Alkaline peroxide etch.

reheated for 400 hr. at 443° C. The alpha has changed to finely banded grains of alpha + kappa (not resolved at the magnification used) and these have partly decomposed to alpha + gamma, but the reaction is far from complete. In one place a eutectoid structure is visible but generally the gamma has precipitated at the grain boundaries only. One end of this same microsample had been squeezed to about 20 per cent

reduction before annealing and this part completely decomposed during the anneal (Fig. 19). Fig. 20 shows a partly decomposed structure in a specimen containing 4.92 per cent Si after annealing at 494° C. for a total of 670 hr. Some of the other samples in this same anneal reacted more quickly. The presence of nuclei of excess gamma does not seem

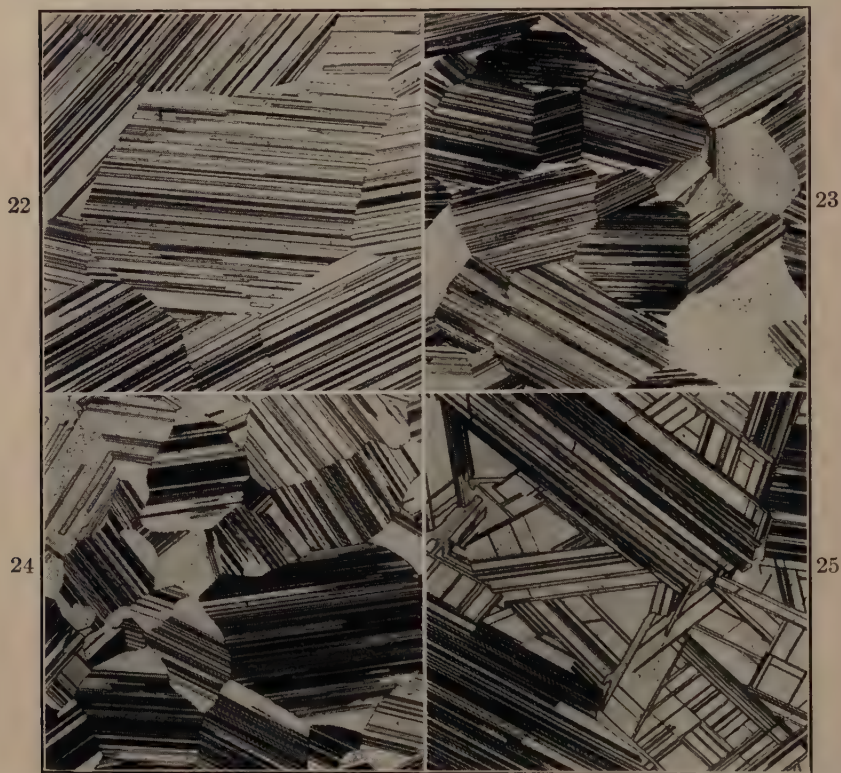


FIG. 22.—ALLOY 3343 (5.22 PER CENT Si). QUENCHED AFTER 228 HOURS AT 743° C. $\alpha + \kappa$. COMPARE WITH FIG. 11.

FIG. 23.—ALLOY 3460 (5.39 PER CENT Si). ANNEALED AT 600° C. TO BECOME HOMOGENEOUS κ , THEN PLACED IN FURNACE AT 775° C. AND HELD 4½ HOURS, QUENCHED $\alpha + \kappa$.

FIG. 24.—ALLOY 3460 (5.39 PER CENT Si). ANNEALED AT 600° C. TO BECOME HOMOGENEOUS κ , THEN SLOWLY HEATED IN 23 HOURS TO 735° C. AND QUENCHED. $\alpha + \kappa$.

FIG. 25.—ALLOY 3458 (4.91 PER CENT Si). SLOWLY COOLED IN 29 HOURS FROM 775° C. (α) TO 600° C. AND QUENCHED.

All $\times 100$. Alkaline peroxide etch.

greatly to accelerate the decomposition of kappa. Precipitation of gamma from supersaturated alpha in alloys below 4.65 per cent Si took place much more readily than the decomposition of kappa in richer alloys.

Fig. 21 shows a type of structure frequently observed in alloys containing over 5.9 per cent Si when reheated at 500° C. or below without

cold-working. Gamma has formed as expected but the residual kappa has given rise to a banded alpha + kappa structure. A little alpha has formed at the grain boundaries in this sample but others showed more extensive alpha patches. Apparently precipitation of hypereutectoid gamma plates took place quickly and the kappa decomposed so slowly that the excess silicon to form gamma could diffuse to the gamma nuclei already present. This left the kappa supersaturated with copper and alpha formed in fine plates just as it does on heating into the alpha + kappa field.

BANDED ALPHA + KAPPA STRUCTURES

The curious banded structure observed when alpha and kappa are in equilibrium, regardless of which one is in greater amount, is worthy of special comment. The platelike form is stable. No amount of annealing will spheroidize either the kappa or alpha phase when they coexist in equilibrium. Compare, for example, Fig. 11 with Fig. 22. Both these photomicrographs are of the same sample, quenched from the same temperature, the former photomicrograph being taken after 41 hr. at 743° C. and the latter after 228 hr. Even though the grains have grown in size, the kappa plates remain parallel and cross the entire grain without having become appreciably thicker than before.

If a sample is rapidly heated or cooled from a homogeneous field into the alpha + kappa region the spacing of the plates becomes finer. Fig. 23 is of a sample that was annealed for 22 hr. at 600° C., to render it homogeneous kappa, then placed in a hot furnace at 775° C. It reached uniform temperature in 1½ min. and was then held for 4½ hr. at this temperature. The bands are almost too fine to resolve at the magnification used and the structure was the same as that of a similar sample held but 2 min. at 775° C. The same alloy heated uniformly in 23 hr. from 600° to 775° C. had the structure of Fig. 24. Very slow cooling from the alpha field into the alpha + kappa zone similarly gave a somewhat coarsened structure, although again no spheroidizing occurred (Fig. 25). Whenever kappa forms from alpha, the kappa bands occur in more than one direction, following the original twins in the alpha grains, but when alpha forms from kappa the bands are parallel throughout the entire grain.

In most two-phase alloys there is sufficient difference of surface energy so that one of the phases tends to reduce its surface area and approach a sphere on annealing. In alpha and kappa, either there is very little difference in surface energy or there is no true interface between the phases, any more than there is at a twinning plane in a homogeneous face-centered cubic lattice. Since kappa possesses a hexagonal structure with very nearly the closest packing, and since copper and silicon have nearly the same effective atomic volume, it may reasonably be supposed that the octahedral planes of the face-centered lattice can

match the basal planes of the hexagonal lattice exactly over a wide range of temperature and composition. The arrangement of the atoms across such an interface would be identical with the arrangement that exists at the twinning plane in a face-centered cubic lattice.

In many systems platelike Widmanstätten figures of considerable stability are formed when orientation relations are correct, and the present system differs from these only in the more exact matching on planes of low indices, whereby it is easier to produce extensive bands. There seems to be no reason why such closely matched lattice planes are unique, and whenever they occur (if the above supposition is correct) the surface energy will be lower for an oriented plate of either phase than for a spheroidized globule.

A number of such banded structures can be found among photomicrographs in the literature, including the eta phase (Cu_3Si) in the copper-silicon system itself. Stockdale¹⁸ has called the author's attention to a similar banded appearance of the delta phase (gamma brass structure) in the copper-aluminum diagram,¹⁹ and this composition range has recently been shown²⁰ to cover three different structures all of which are closely related.

SUMMARY

By microscopic examination of quenched samples, the domain of the new kappa phase adjacent to alpha in the copper-silicon system has been determined. It is formed by a peritectoid reaction of alpha and beta at 842° C. and then contains 5.9 per cent Si by weight ($= \text{Cu}_7\text{Si}$). It decomposes eutectoidally at 552° C., when it contains 5.2 per cent Si ($= \text{Cu}_8\text{Si}$). On the silicon-rich side it extends to 6.85 per cent ($= \text{Cu}_6\text{Si}$) at 785° C. and 6.95 per cent Si at 729° C. The maximum extent of the alpha phase is to 5.3 per cent at 842°, decreasing to 4.65 per cent ($= \text{Cu}_9\text{Si}$) at 552° C. and less at lower temperatures.

Most unusual microstructures are observed in the alpha + kappa field, for the two phases exist as twinlike plates and do not spheroidize even when grain growth occurs following working and long annealing. The decomposition of kappa to alpha + gamma below 552° C. is extremely slow unless the samples are cold-worked.

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DISCUSSION

(A. Allan Bates presiding)

M. G. CORSON,* New York, N. Y.—I am glad Dr. Smith did not stop self-contentedly after having proposed his diagram of 1928 and I agree completely with his conclusions of today. I am sure they will produce an impression upon the theorists of the equilibrium diagram and will radically contribute to the change of our ideas regarding the alpha and the beta phases in general.

First of all, the old term "polyhedral grains" will have to be scrutinized and modified, if not entirely eliminated. It can be proved by a very simple geometric construction that no polyhedron, cross-sectioned and etched, can produce a *polyhedral aspect* in a photograph. And it is my deep conviction that polyhedral effects are caused by striations just as in a 5.2 per cent copper-silicon alloy, but that the striation is so fine as to produce the appearance of a homogeneous plane. In other words, a dark plane in a photomicrograph of alpha brass is due to that fine striation along the proper direction, a bright plane occurring where no striae are cut through. In my conception, not even a 20 per cent brass is a homogeneous phase but is formed of

* Consulting Engineer.

orderly plates of two phases—one nearly pure copper, the second an X phase much richer in zinc. To the presence of that second phase I ascribe the phenomena of season cracking in brasses and aluminum bronzes, as well as the extraordinary changes in electric conductivity noticed in tin bronzes.

In my paper of 1928 on iron-silicon alloys,²¹ I mentioned the appearance of some specific structures, which I called "barley shells" in alloys containing from 6 to 12 per cent Si. I wish to restate again my conviction that iron-silicon alloys of the range that I investigated were formed of two phases differing in composition but not in the lattice shape, which are compelled by their nature to form the specific patterns. And I am sure that iron-aluminum alloys as well as copper-phosphorus, copper-antimony and copper-arsenic alloys will display analogous patterns—either plain striae or barley shells—on proper etching.

Whether the kappa phase has a hexagonal lattice, as the Japanese investigators claim, I do not know. But granted this to be true, it explains why the kappa phase embrittles but does not strengthen copper. The reason is that only cubically crystallizing substances plus rhombohedral and specific rhombic ones can be fitted into a lattice of copper without causing impossibly high stresses. So all others are either retained in solution (aluminum-magnesium alloys) or ejected to the grain boundaries, or compelled to form plates among plates of the alpha solution with an intimate share of the adjoining atoms (no true interfaces).

Copper-silicon alloys with 6 to 7 per cent Si are extremely plastic at high temperatures. They extrude easily. Allowed to cool in air they become brittle (eutectoidal dissociation of the kappa). Quenched they retain a ductility of 25 per cent plus a strength of over 100,000 lb. per sq. inch.

And, by the way, I wish to ask the X-ray specialists whether the "kappa" may not be after all a body-centered cube like beta brass, incidentally appearing "hexagonal" because existing in the shape of plates of a strictly octahedral orientation?

D. STOCKDALE,* Cambridge, England.—That the fixed points on this diagram fall at simple ratios is a matter of great interest. I have been working on simple ratios for some time, and as equilibrium diagrams become more accurately known so do I find that more systems conform to the empirical rules I have put forward.²² The simplest of these is that if a silver-rich or copper-rich alpha phase is in such a state that a suitable, small change in temperature can cause one new phase to appear and also a small increase in concentration of the solute will cause the appearance of a second, new phase, the ratio by number of solute to solvent atoms is simple. There are three such points on this diagram (4.65 Si, 552°), (5.3 Si, 842°) and (5.25 Si, 852°). (See Fig. 5.) Ratios of 1 Si:9 Cu and 1 Si:8 Cu require respectively 4.67 and 5.23 wt. per cent Si. Thus there is a general conformity with the rule. The rule, strictly applied, demands that the $\alpha/\alpha + \beta$ phase boundary be vertical, because two compositions so close together as 5.3 and 5.25 wt. per cent Si cannot both be expressed as simple ratios.

Another rule is that in a binary eutectic at the eutectic temperature, the ratios of the atoms, irrespective of their kind, in the two phases are simple.²² Peritectic and eutectoid reactions closely resemble eutectic reactions, and the eutectic rule should be applicable to them. In this part of the copper-silicon system there are five such reactions. (See Fig. 5 and list at foot of page 321.) Unfortunately, in considering eutectic reactions three experimental points must be examined, each one of which is subject to small experimental errors. Possibly the best method of approach is to

²¹ *Trans. A.I.M.E.* (1928) **80**, 249.

* Lecturer, University of Cambridge.

²² *Proc. Roy. Soc.* (1935) **152-A**, 81.

assume that only the peritectic and eutectoid compositions are subject to experimental error and that all the other points are correct. We can then draw up a table for the reactions given on p. 321 (Table 5).

TABLE 5.—*Reactions on Page 321*

Reaction	Suggested Ratio	Eutectoid or Peritectoid Composition, Atomic Per Cent Si		Difference, Atomic Per Cent Si
		Found	Required by Ratio	
$\alpha + \text{liq.} \rightleftharpoons \beta$	2:3	14.2	14.06	+0.14
$\alpha + \beta \rightleftharpoons \kappa$	1:2	12.45	12.32	+0.13
$\kappa + \delta \rightleftharpoons \beta$	1:1	16.0	15.95	+0.05
$\kappa + \delta \rightleftharpoons \gamma$	1:5	17.1	17.13	-0.03
$\alpha + \gamma \rightleftharpoons \kappa$	1:6	11.05	10.97	+0.08

Thus the rule in three cases works out correctly when allowance is made for the author's estimated experimental error of 0.1 atomic per cent and under the conditions laid down. An allowance of 0.1 per cent suitably used, on each of the three points, will, obviously, cause all the reactions to conform.

Because of the large difference between the atomic weights of silicon and copper, this system is unsuitable for use in attempting to prove simple-ratio rules, and to some extent the remarkable agreement shown in Table 5 may be a matter of chance. The probability that three numbers of these orders of magnitude chosen at random will give a simple ratio when each may be adjusted by 0.1 atomic per cent is comparatively high.

As Dr. Smith points out, there are simple ratios at other fixed points on the diagram. These must be linked in some way to those described above, and it may even be that a rule similar to the alpha-solid solution rule can be formulated for secondary solid solutions of the kappa type, in which case the second rule given above may have to be modified when applied to peritectic and eutectoid reactions.

A. G. H. ANDERSEN,* Maspeth, N. Y.—There can be no doubt that the banded structure Dr. Smith has so well brought out is characteristic of the two-phase region, after the alloys have been cold-worked. It is, however, my own unpleasant experience that in alloys not cold-worked the usefulness of this habit of coexisting alpha and kappa to assume a plate-form structure is not very high. This may be owing partly to this habit itself and partly to reaction rates.

Dr. Smith's statement that in castings the kappa phase is largely segregated in the last part of the dendrite to solidify is in accord with our own observations and expectations. Often gamma was associated with this kappa and the alloys are both hot short and cold short.

The transformation between alpha and kappa can occur with a minimum of atomic motions and rearrangement of the atoms, when the (111) planes in the alpha phase becomes the (002) planes of the kappa phase (however, with increase in their spacing) and the cube diagonal becomes the hexagonal axis with a length roughly $\frac{2}{3}$ times the cube axis. The interatomic distances on the respective planes do not coincide. A measure of these distances are the (220) spacings in the alpha phase

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and the (110) spacings in the kappa phase. These spacings I have calculated from X-ray data, and these show that the spacings in the kappa phase are about 0.08 per cent smaller than in the alpha phase, and that this ratio varies. There are, therefore, no common or shared lattice positions on these respective planes. That interfaces related in this manner to the structures and atomic spacings on both sides of the boundary may have different properties from, say, the interfaces between alpha and gamma, is an entirely reasonable assumption. It seems to me, however, that this interface still should be called a true interface. For not only do the equilibria of the phases conform to the phase rule, but the interface marks a boundary on either side of which the atoms are arranged in space lattices of different symmetry, with different interatomic distances and with different atomic ratios of copper and silicon atoms.

C. H. SAMANS,* State College, Pa.—In connection with the beautifully banded structures of alpha and kappa shown by Dr. Smith, a further comment seems pertinent with regard to the mechanism of their formation.

The extremely straight sides of the bands suggest strongly that they are formed directly from the alpha by a shearing process similar to that used to explain the formation of twins in face-centered cubic metals. This is entirely feasible, since a similar transformation, without however the complicating factor of diffusion, has already been found by Dehlinger, Oswald, and Bumm²³ in their work on the face-centered cubic-hexagonal allotropic transformation in cobalt. A simple shear on (111) planes in a [112] direction, in which every plane of atoms shears uniformly and for a definite distance over every other plane, gives the twinned arrangement, while an equal magnitude of shear in which the planes move in pairs instead of singly gives the hexagonal arrangement. From this viewpoint two possibilities arise:

First, the silicon could tend to segregate in regions parallel to octahedral planes in the alpha lattice or to basal planes in the kappa lattice, and to transform *in situ* in these regions to form the bands of the second phase. However, the X-ray parameter data in Mr. Andersen's paper† seems to make this possibility rather improbable.

Second, the shearing processes could be initiated in regions that are sufficiently rich in silicon because of the chance distribution of that element, and are then propagated in a regular manner by the diffusion of silicon atoms from the surrounding regions to those which are within the "sheared band." These regions then would change their dimensions to conform to those of their equilibrium concentration.

The second explanation seems to be the more probable, although, admittedly, there is no experimental evidence to substantiate it other than the remarkable straightness of the bands. I find difficulty in explaining the transformation satisfactorily by means of the so-called Widmanstätten mechanism—i.e., a pure interface reaction—unless that is presumed to take place by a shearing process.

C. S. SMITH (author's reply).—I deeply appreciate Mr. Corson's comment on my paper. Mr. Corson's classic work opened up entirely new fields of metallography and if I had paid the attention to his 1927 paper that it deserved I would not have made the mistake of overlooking the kappa phase in 1928.

The question of the workability of the kappa alloys is in doubt. While Sautner was able to prepare wire from kappa, my own attempts to roll it either hot or cold resulted in failure unless it was mixed with a good proportion of alpha. It can be extruded, as Mr. Corson mentions. The beta phase, according to my experience, is very plastic. It decomposes rapidly on cooling but it is possible to retain it without visible decomposition by extremely rapid quenching.

* The Pennsylvania State College.

²³ Dehlinger, Oswald and Bumm: *Ztsch. Metallkunde* (1933) **25**, 62.

† Page 334, this volume.

Dr. Stockdale's discussion of the simple ratios at the various peritectoid and eutectoid points is most interesting. His analysis of this system together with the others that he has previously studied provide quite convincing evidence that the simple ratio scheme generally determines the relation of phases at fixed points.

I welcome Dr. Andersen's discussion. My opinion on the points wherein we disagree is given in my discussion on his paper (page 351). I feel that the interatomic distances in the (111) and (002) planes of alpha and kappa phases respectively must be identical in order to account for the observed microstructures, and think the small divergence actually found results from the fact that the X-ray studies must be made at room temperatures and hence do not precisely represent conditions before quenching. Whether or not there is an interface between oriented kappa and alpha depends on definitions. It seems likely that there is no more surface energy associated with this junction than there is with a twin boundary or with the boundary between an ordered and unordered zone in a solid solution. The present case differs from these only because there are other planes where no match is possible, and these provide the boundary that determines the behavior according to the phase rule. I have no evidence to support my belief and the question must await further study.

The Alpha Solubility Limit and the First Intermediary Phase in the Copper-silicon System

BY A. G. H. ANDERSEN,* MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

DURING an investigation of the copper-rich portion of the copper-silicon-iron system as part of an extensive research program on P.M.G. alloys, which was begun in 1937 in the research laboratory of the Phelps Dodge Corporation, it became apparent that the binary copper-silicon system below 7 per cent Si needed revision, therefore an investigation was undertaken. Both X-ray methods and microscopic technique were employed.

Despite the many investigations that have the clarification of this system as their object, no two successive reports on the system have agreed in placement of the alpha-phase solubility limit, and uncertainty about the secondary phase first to appear has been voiced several times.^{3,4,5}

It was therefore not surprising, when T. Isawa's⁶ and M. Okamoto's⁷ works were reported at the time we were finishing up our experimental work, to find essential disagreement between their results and ours. But when C. S. Smith's latest work on the copper-silicon system⁸ was published just as we were finishing our laboratory report, it was indeed gratifying to find that the latter's diagram and ours checked in all essential features, except the temperature of the peritectoid line above 830° C.

Many attempts were made to retain the beta phase during the present investigation, but none was successful. Isawa,⁶ however, reports that he has been able to obtain X-ray photograms of the beta phase. The structure, he states, is body-centered cubic with a lattice constant of 2.848 Å. at 7.2 per cent Si.

Okamoto⁷ and Smith⁸ both use the designation Kappa for the hexagonal phase, and to avoid confusion this designation will be adhered to in the present paper.

PREPARATION OF SAMPLES

The alloys were melted in vacuum in a high-frequency furnace from copper cathodes containing 99.98 per cent Cu, and specially refined silicon supplied by The Electro Metallurgical Co. This silicon is stated

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³ References are at the end of the paper.

to contain 99.85 per cent Si. Alundum crucibles were used except for a few melts, which were made in graphite crucibles. The ingots were annealed in vacuum at 800°C. for at least one week, after the surface layer of metal had been discarded.

Samples for chemical analysis were made by taking a lathe cut from the bottom of the ingots, using a Carboloy cutting tool. The X-ray samples were taken directly under the lathe-cut surface by filing, due precaution being taken against contamination.

CHEMICAL ANALYSIS

Determinations of copper, silicon and iron-aluminum combined were made on most of the alloys. A few alloys were analyzed spectrographically.* Many elements were found to be present in minute amounts. The amounts of iron and aluminum were comparatively large. Iron was present up to 0.05 per cent and the aluminum content probably was not higher than 0.1 per cent. It was ascertained that at least part of the aluminum was present as alumina, in all probability picked up from the alundum crucibles. The alloys melted in graphite crucibles contained 0.015 per cent Fe and 0.01 and 0.02 per cent Al. The effect of any of these amounts of aluminum on the equilibria was not noticeable.

X-RAY ANALYSIS

Solid specimens weighing about 5 grams were cut from the ingots next to the sample for chemical analysis. Whenever possible, these

TABLE 1.—*Chemical Analysis and Lattice Constants*

Alloy No.	Silicon		Lattice Constants, Å.	Alloy No.	Silicon		Lattice Constants, Å.
	Per Cent by Weight	Atomic Per Cent			Per Cent by Weight	Atomic Per Cent	
18	6.15	12.94		34	4.84	10.33	3.61446
19	5.08	10.83	3.61474	54	5.47	11.59	3.61534
20	4.38	9.40	3.61385	55	4.73	10.11	3.61426
21	3.01	6.61	3.61223	56	5.98	12.60	
22	1.99	4.40	3.61048	57	6.69	14.00	
23	0.98	2.19	3.60907	58	5.60	11.85	
24	0.48	1.09	3.60833	60	5.36	11.38	3.61501
29	8.60	17.57		61	4.65	9.95	3.61412
30	7.84	16.16		64	3.81	8.25	3.61310
31	9.10	18.48		65 ^a	5.73	12.10	
32	6.13	12.87		66 ^a	5.25	11.15	
33	7.02	14.60		67 ^b	7.6	15.71	

^a Melted in graphite crucibles.

^b Not analyzed.

* This work was done by Lucius Pitkin, Inc.

specimens were treated so as to yield a homogeneous solid solution, before filings were taken for X-ray samples. The various treatments consisted in quenchings from 810° to 830° C., after annealing for 30 to 70 hr., generally about 50 hr. Some of the solid samples were annealed and quenched from the same temperature as that at which the filings taken from them subsequently were treated. The powders were sealed up in evacuated silica tubes of $\frac{1}{8}$ -in. bore, and brought as nearly as possible to a state of equilibrium by heating at standard temperatures

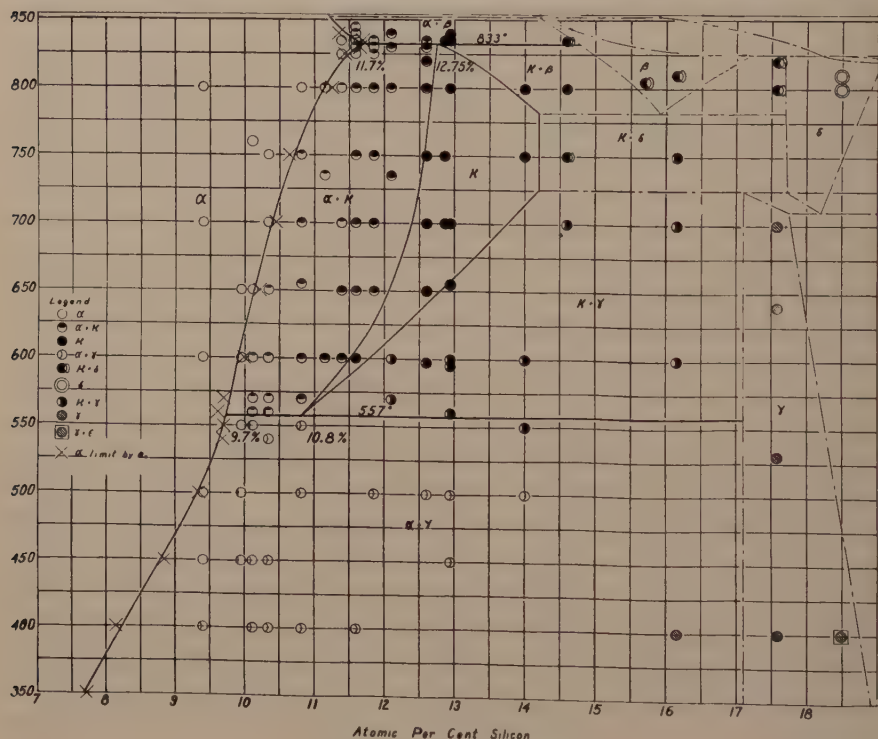


FIG. 1.—X-RAY RESULTS.

for varying lengths of time. At 700° C. and above, annealing periods of 20 hr. to 3 days were used, and at 600° C. and below, periods of 5 to 48 days were generally used. These treatments are specified in a table in the appendix, in which also is found other detailed information of the X-ray work. The samples were quenched by automatically breaking the tubes under water.

The line patterns for identification were obtained by a Debye-Scherrer camera of 10-cm. radius and by a nonsymmetric-focusing type of camera. All films used for measuring lattice constants were taken in a focusing type of camera of high dispersion. The two cameras last named were designed by E. R. Jette.

The wave lengths used in the calculations of the lattice constants are as follows:

Fe: $\lambda_{\alpha_1} = 1.932076$	$\lambda_{\alpha_2} = 1.936012$	$\lambda_{\beta} = 1.753013$
Co: $\lambda_{\alpha_1} = 1.78529$	$\lambda_{\alpha_2} = 1.78919$	$\lambda_{\beta} = 1.61744$

RESULTS OF X-RAY ANALYSIS

Phase Identification by X-ray Patterns.—The photograms gave the line patterns of four distinct structures; viz.: (1) the copper solid-solution structure, (2) a hexagonal close-packed structure apparently identical with the phase described by Arrhenius and Westgren⁹ but not located in Smith's beta region as assumed by these authors; (3) the gamma structure, and (4) the delta structure.

Fig. 1 shows the composition-temperature fields where the various phases were located. Fig. 2 shows photograms of the alpha phase, kappa phase and gamma phase. Many reflections of the alpha phase and kappa phase coincide.

In some instances three phases were found together in the same powder sample, even after meticulous care had been exercised in the preparation of the samples. This occurred particularly at temperatures close to that of the eutectoid change of 557° C., and is mainly owing to the slow rates at which these alloys approach equilibria, but also, undoubtedly, in some cases to the difficulty of obtaining powders of uniform composition. In this connection it should be noted that, owing to the slowness of the reaction, the eutectoid transformation could not be detected by cooling curves.

Lattice Constants of the Alpha-copper Lattice.—The a_0 values are given in Table 1. Within the limits of experimental error the lattice-constant function is a straight line expressed by $a_0 = 3.6077 + 0.00065 \times C$ where C is atomic per cent silicon. A plot of a_0 values is shown in Fig. 3, which include data on the lattice constants of two-phase alloys at various temperatures. These values are at variance with those determined in some other laboratories.^{6,10} Information on the latter is given in the Appendix. At room temperature a_0 varies with temperature at the rate of 0.00006 Å. per degree Centigrade.

A summary of lattice constants of two-phase alloys is given in Table 2.

DISCUSSION OF X-RAY DATA

Fig. 1 shows diagrammatically, as revealed by the photograms, the relative amounts of phases present in the alloys after various heat-treatments. The alpha-phase boundary above 550° C. is fairly well delineated by the phase-identification points of the X-ray films, and below 550° C. it is outlined by means of photomicrography as well as by the X-ray patterns. The temperature of transition from alpha to alpha + kappa



FIG. 2.—PHOTOGRAMS OF PRINCIPAL PHASES.
Reduced approximately $2\frac{1}{2}$ times in reproduction.

can be clearly seen to be lower the smaller the silicon content of the alloy. At 560° C. alloys 55 and 34 show very weak kappa-phase lines together with the alpha-phase lines. At 550° C. and below, these alloys show alpha-phase and gamma-phase lines. Alloy No. 61 at 550° C. does not show any gamma-phase lines. The microscopic work, as illustrated in Fig. 4, shows that all these alloys contain gamma in this temperature region (550° C.). That no gamma-phase lines actually show on the

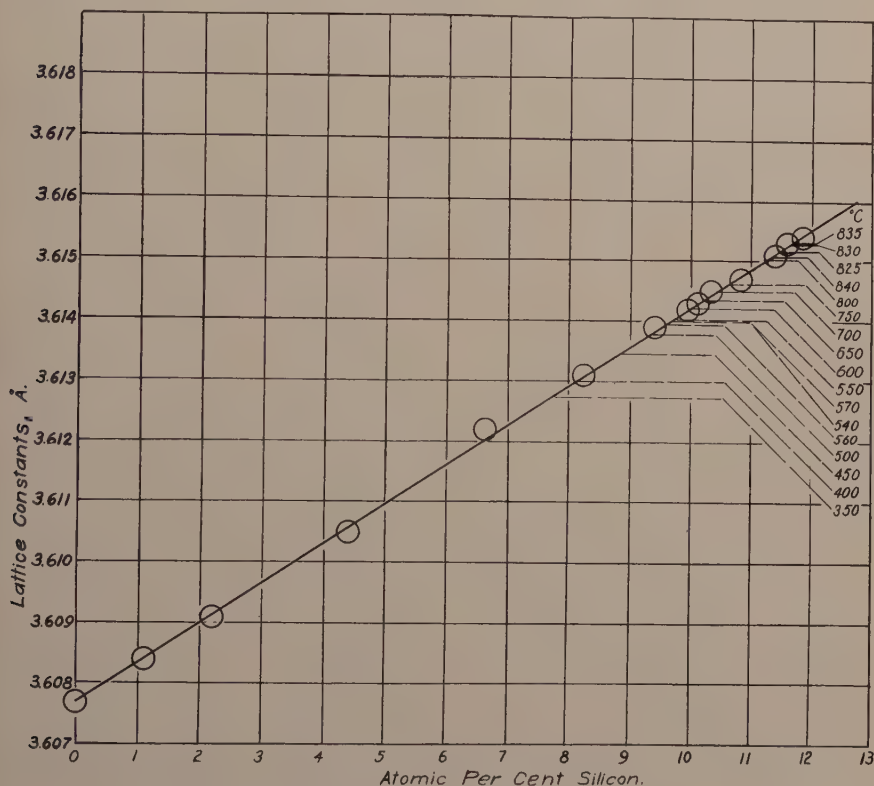


FIG. 3.—LATTICE CONSTANTS OF THE ALPHA PHASE.

X-ray film of No. 61 is due, undoubtedly, to the small amount of gamma actually present in that alloy. Such a condition is quite common in X-ray work as occasionally 0.5 per cent or even more of a secondary phase must be present before its reflections become visible on the films.

As mentioned before, none of our photograms show the beta phase. This is in agreement with Smith's statement² that this phase cannot be retained by quenching. The beta phase breaks down during quenching into kappa and delta. In many of our photograms of alloys that under the microscope show the delta-kappa eutectoid, only the kappa lines from this are visible. These alloys are easily recognizable on Fig. 1.

Alloy No. 54 is of especial interest. At 845° and 840° C., this alloy shows lines due to the alpha phase together with weak lines due to the kappa phase. At 835° C. and at 830° C., virtually only alpha-phase lines can be found. But at 825° C. the kappa-phase lines reappear

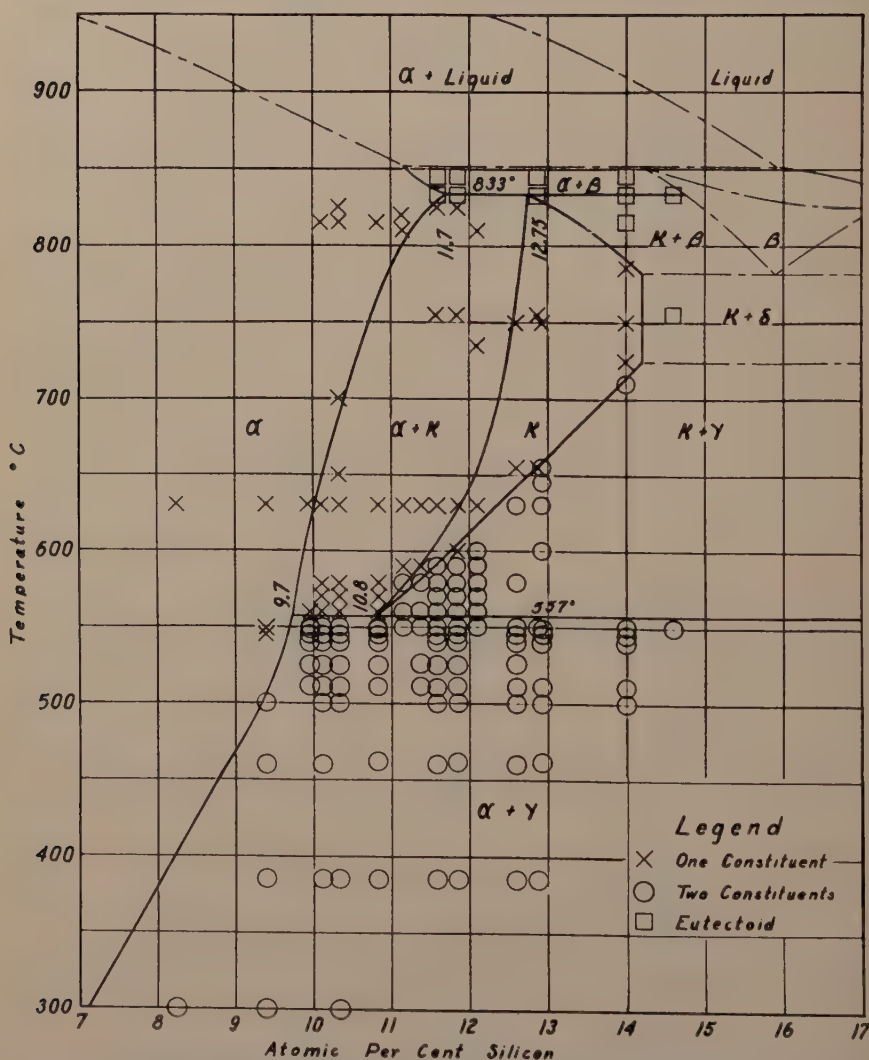


FIG. 4.—PHASES ACCORDING TO MICROSCOPIC OBSERVATION. The square symbol indicates the presence of some eutectoid in a matrix of either alpha or kappa.

weakly, and at 800° C. more strongly. At still lower temperatures the kappa-phase lines become gradually stronger, until at 600° C. the alpha-phase lines found are very weak. At the still lower temperature of 550° C., gamma-and-alpha-phase lines, together with weak kappa-

phase lines are present. At 400° C. only the two former sets of lines are present. There is thus a strong proof that the alpha-phase boundary must show an abrupt change of direction between 830° and 835° C. and it is also indicated that in the temperature range between 550° and 570° C.

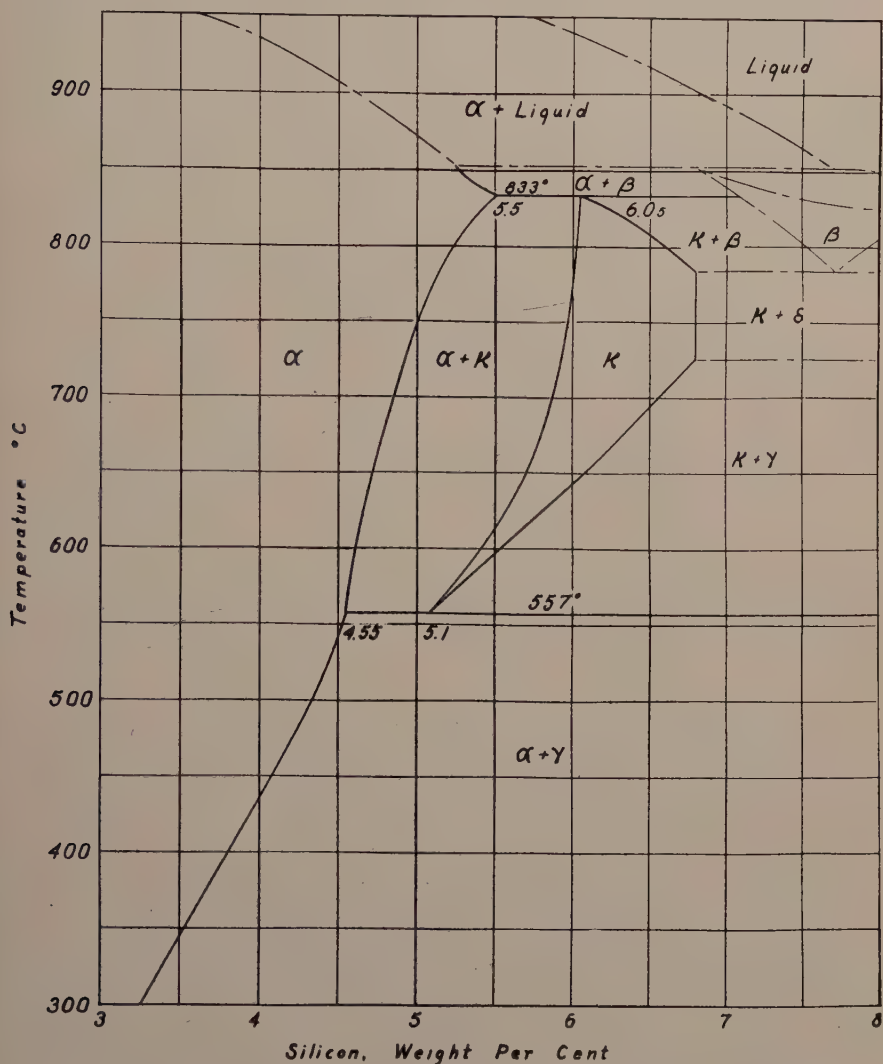


FIG. 5.—COPPER-SILICON DIAGRAM BETWEEN 3 AND 8 PER CENT BY WEIGHT.

there occurs a transition from kappa to alpha. From these results alone, a horizontal line on the diagram at 560° C. could be drawn with fair confidence. However, in this region a number of alloys, not marked on the diagram, since they are manifestly not in equilibrium, show three phases. These are Nos. 60 and 66, which at 540° C. show weak lines of

kappa phase in addition to strong alpha-phase and weak gamma-phase lines; at 560° C. the alpha-phase lines are weak and the kappa-phase lines strong.

In addition to these unstable alloys, Nos. 66 and 54 at 570° show alpha-phase and kappa-phase lines. It is quite probable that these alloys had not attained equilibrium. Additional reasons for considering the state shown by Nos. 54 and 66 at 570° C. as unstable lie in the fact that the microscopic work shows that the boundary for the occurrence of the gamma phase extends to the left of these alloys at and below 570° C.

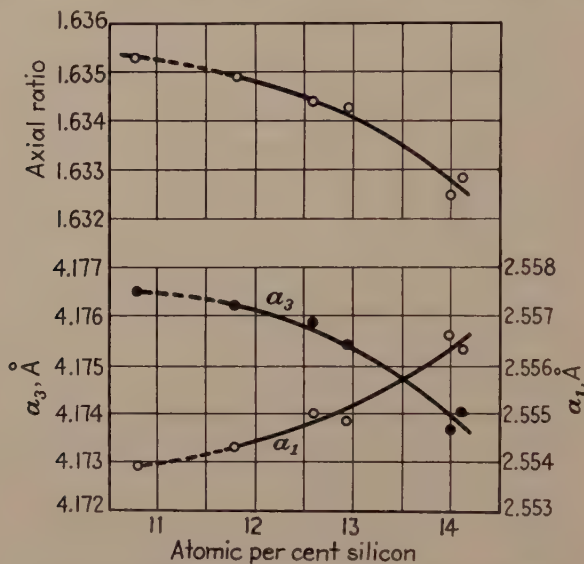


FIG. 6.—LATTICE CONSTANTS OF THE KAPPA PHASE.

and including No. 60 at 11.38 per cent Si below 578° C. From the relative distribution of the phases in the group of unstable alloys, it is immediately probable that at 570° C. the stable phases in Nos. 54 and 60 are kappa and gamma. This is clearly indicated by alloys 61, 55, 34, 19 and 65, which tend to show that below 560° C. the kappa phase is not stable while above 570° C. that phase is stable. Essentially the same state is shown by the microscopical examination of the alloys in this region. Thus, alloys Nos. 19 and 34 show that the gamma phase is stable below 560° C., while it does not occur in these alloys at 570° C. and above. This very strongly points to a transition line close to 560° C. Therefore, below approximately 560° C. alpha and gamma are stable, at 570° C. kappa and gamma are stable in alloys of silicon content higher than that of No. 66 (11.15 atomic per cent Si), and kappa and alpha in alloys of silicon content lower than that of No. 19 (10.82 atomic per cent Si). These conditions, according to the phase rule, can prevail only when the

TABLE 2.—Alpha Copper Lattice Constants and Solubility Limits

ALLOY No.	64	120	61	55	34	19	66	60	54	58	65	ANGSTROM UNITS	SOLUBILITY LIMIT, ATOMIC PER CENT Si
PER CENT	8.25	9.40	9.95	10.11	10.33	10.82	11.15	11.38	11.59	11.85	12.10		
TEMPERA- TURE, DEG. C.													
840									3.61520		3.61497	3.61509	11.35
835								3.61506	3.61518	3.6153		3.61530	11.70
830									3.61550	3.6154	3.61515	3.61528	11.65
825								3.61496	3.61520	3.61507		3.61514	11.43
800	3.61330	3.61390				3.61474		3.61514	3.61475	3.61518		3.61502	11.25
750				3.61426	3.61445	3.61470			3.61455	3.61461		3.61462	10.63
700		3.61380			3.61448	3.61470			3.61444	3.61437		3.61450	10.45
650			3.61417	3.61412	3.61426	3.61438			3.61440	3.61440		3.61436	10.22
600			3.61406	3.61434	3.61431	3.61410		3.61410				3.61421	9.99
570				3.61400	3.61400							3.61400	9.69
560				3.61380	3.61410		$\alpha + \kappa$					3.61395	9.61
550			3.61383	3.61395	3.61393	3.61416	$\alpha + \gamma$		3.61420			3.61401	9.69
540					3.61400		3.61410	3.61400				3.61400	9.68
500	3.61290	3.61370	3.61373		3.61385	3.61365		3.61382		3.61398		3.61378	9.34
450		3.61365	3.61328	3.61352	3.61340							3.61345	8.84
400		3.61300		3.61284	3.61300	3.61290						3.61300	8.14
350	3.61274				3.61272				3.61320			3.61272	7.71

Although the individual lattice constants are known to the limit of $\pm 0.0002\text{\AA}$, it has been found desirable to carry the calculations to the fifth decimal place.

homogeneous kappa region extends down below 560° C. between these two compositions, to a eutectoid point. The location of this is established by the contour of the kappa region, which is determined microscopically from the first appearance of the gamma phase in the metallographic specimens, as shown in Fig. 3. The eutectoid point is thus probably close to 10.8 atomic per cent Si or 5.15 weight per cent.

Alpha-phase Boundary

The lattice constants of the alpha phase in two-phase alloys were utilized for the establishment of the solid solubility limit. Owing to the small change in the lattice constants of the alpha phase with composition, the lattice constants of the two-phase alloys must be known with an unusual degree of precision, if ordinary precision is to be obtained on the position and course of the phase boundary. In the Appendix all alpha-phase lattice constants of two-phase alloys are included. A summary of these is given in Table 2. Fig. 1 shows the solubility limits at various temperatures, which correspond to these data and the representative curves drawn between them. The deviation of each individual point in general is about ± 0.1 atomic per cent. The separate portions of the curve distinguishing between kappa and gamma regions are made to meet between 550° and 560° C. and 9.7 atomic per cent in order to satisfy the phase-identification work. The course of the curve at high temperature may be seen from the diagram. There is a sharp peak on the curve at 11.8 atomic per cent and a temperature coincident with a peritectoid reaction line. The temperature of this peritectoid reaction by which kappa is formed from alpha and beta is established at 833° C. from the differentials of the lattice constants at 835°, 830° and 825° C. As we do not know the temperatures closer than $\pm 2^\circ$ C. over the long annealing periods used, this is substantially the same temperature as that which Smith^{1,8} in his earlier works shows as a short horizontal or inflection on his alpha-phase boundary.

Lattice Constants of the Kappa Phase

In 1931 Arrhenius and Westgren⁹ gave the following values: $a_1 = 2.588$ Å., $a_3 = 4.176$ Å., $c = 1.633$ for the hexagonal close-packed structure they assigned to Smith's beta region. T. Isawa, in 1938, gave the values of: $a_1 = 2.5528$, $a_3 = 4.1523$, $c = 1.6255$ for the same structure.

From a number of measurements we have established a definite change in the dimensions of the elementary cell of the kappa phase with silicon content. Table 3 shows the lattice constants as well as the location of the respective alloys on the composition-temperature diagram. A diagram of the lattice constants is shown in Fig. 6.

The axial ratio also varies with the silicon content. The rate of change varies, and increases from 0.02 per cent per atomic per cent Si at

11 atomic per cent Si to 0.15 per cent per atomic per cent Si at 14 atomic per cent Si. The total decrease in axial ratio between 11 and 14 atomic per cent is 0.18 per cent.* Further data and discussion are found in the Appendix.

TABLE 3.—*Lattice Constants of the Kappa Phase*

Alloy No.	Heat-treatment Temperature, Deg. C.	Kappa Phase, Atomic Per Cent Si	Lattice Constants		
			a_1	a_2	c
66 ^a	560	10.9	2.5539	4.1765	1.6353
58	600	11.8	2.5543	4.1762	1.6349
56	650	12.6	2.5550	4.1759	1.6344
18	700	12.95	2.5549	4.1755	1.6343
18	800	12.95	2.5548	4.1753	1.6342
57	750	14.00	2.5566	4.1737	1.6325
33	750	14.60	2.5563	4.1741	1.6328

^a Two phases, kappa and gamma, present. The composition of the kappa phase inferred from the diagram of Fig. 1.

MICROGRAPHIC IDENTIFICATION OF PHASES

The microscopic search falls in two sections: (1) determination of the alpha + kappa range and (2) determination of the boundaries for the existence of the gamma phase.

1. This part included checking of the conditions above 800° C., where occurs the beta phase, which upon quenching breaks down into kappa + delta. No certain means of distinguishing between the alpha and the kappa phase by microscopic and etching methods were found. In general it can be said that it is easy enough to distinguish between alpha solid solution and the kappa phase because the alpha phase is isotropic whereas the kappa phase is anisotropic and shows high birefringence and interference colors under crossed Nicols. But practically the criterion is useless because as the silicon content approaches the alpha boundary the alpha solid solutions gradually become anisotropic and may give quite high colors. The habits of the two crystal phases give no clear indication of the phase boundary, unless perhaps after carefully controlled cold-work and recrystallization.

The alpha + kappa structures are apt to show heavily striated grains, but so often do the alpha structures alone when the silicon is high. Homogeneous kappa does not show such pronounced striations; but alloys in the alpha + kappa regions may or may not show striation and twinning, depending upon mechanical work and heat-treatment. It

* At 13.85 atomic per cent silicon the closest packing is attained ($R = 1.633$). At this point the ratio of silicon atoms to copper atoms 1:6.2, and the electron concentration is 1.415.

thus seems that distinction between alpha and kappa + alpha and between kappa + alpha and kappa by means of the microscope will require the working out of a standard for mechanical work and heat-treatment and observation of any difference, structurally, in the response to this treatment.

2. This required simply detection of the presence or absence of the gamma phase in heat-treated alloys. The gamma phase after etching has a characteristic pale blue color, easily distinguishable from the red of the matrix by eye in the microscope. The color difference is not, however, well fixed on an orthochromatic photographic plate. The amounts of gamma produced by annealing temperatures below the eutectoid line were in many cases obviously subequilibrium. The mere appearance

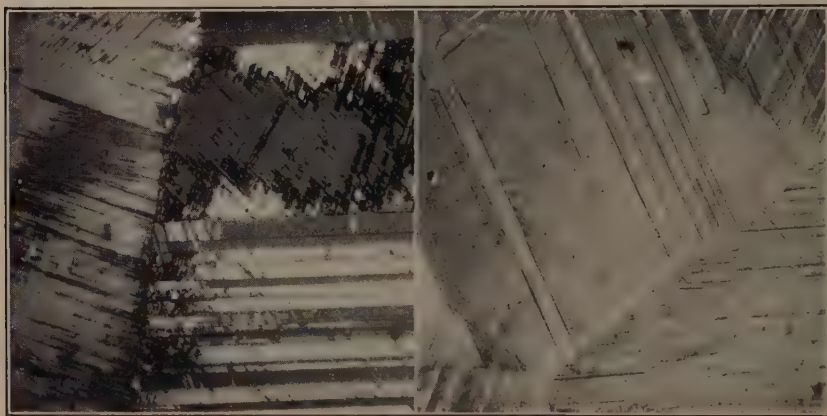


FIG. 7.

FIG. 8.

FIG. 7.—ALLOY NO. 19. QUENCHED AFTER 50 HOURS AT 815° C. POLARIZED LIGHT. ALPHA.

FIG. 8.—ALLOY NO. 61. QUENCHED AFTER 48 HOURS AT 815° C. POLARIZED LIGHT. ALPHA.

Chemical analysis in Table 1. Original magnification, 200. Reduced approximately $\frac{1}{3}$ in reproduction.

Etchant: Potassium bichromate and sulphuric acid. Smith's modification.

of gamma, of course, indicates the transition line. Fig. 13 illustrates such a case.

Fig. 4 shows the results of the micrographic analysis. A detailed account of these are given in the Appendix. The lengths of the annealing periods were usually 3 to 12 days; a number of the specimens were hammered cold before heat-treatment, but as it soon was found that castings of higher silicon contents broke up during hammering, the procedure was discontinued.

Discussion of the Micrographic Work

Despite the fact that the alpha phase is cubic or isometric, with high silicon concentration, it is nevertheless seen to be anisotropic when viewed

in polarized light with crossed Nicols. Figs. 7 and 8 illustrate this clearly. In addition, both photomicrographs show striated grains and heavy twinning.

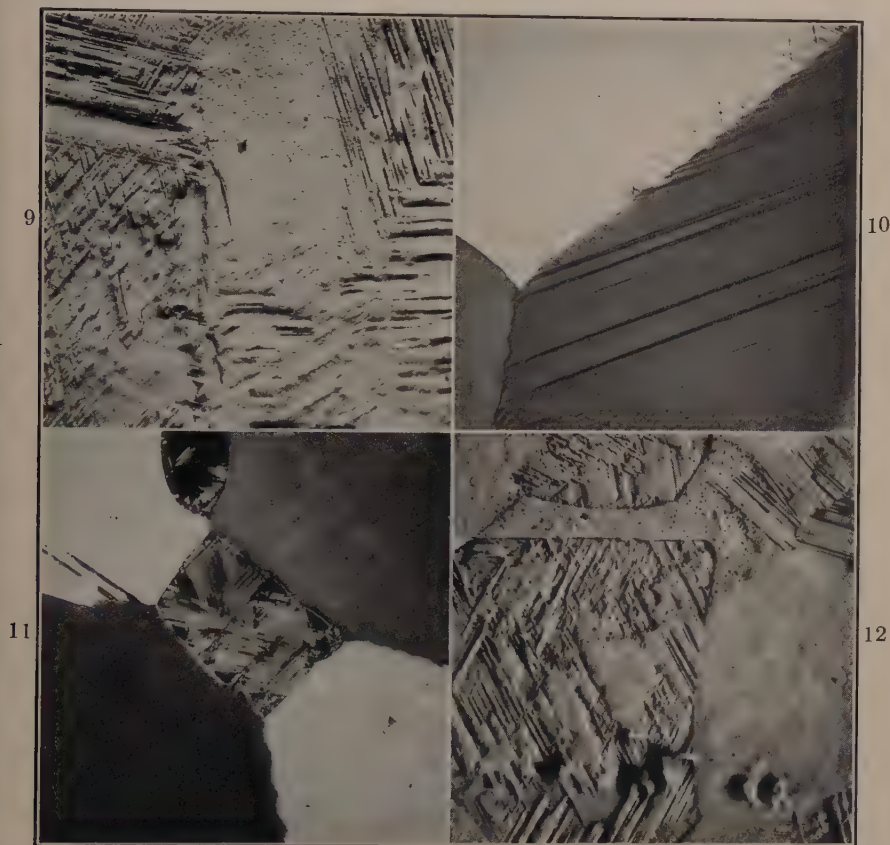


FIG. 9.—ALLOY No. 60. QUENCHED AFTER 72 HOURS AT 820° C. OBLIQUE ILLUMINATION. $\times 500$. ALPHA.

FIG. 10.—ALLOY No. 57. QUENCHED AFTER 72 HOURS AT 750° C. POLARIZED LIGHT. $\times 200$. KAPPA.

FIG. 11.—ALLOY No. 65. QUENCHED AFTER 96 HOURS AT 810° C. POLARIZED LIGHT. $\times 200$. ALPHA AND KAPPA.

FIG. 12.—ALLOY No. 54. QUENCHED AFTER 42 HOURS AT 825° C. OBLIQUE ILLUMINATION. $\times 500$.

Chemical analysis in Table 1. Original magnifications given; reduced approximately $\frac{1}{2}$ in reproduction.

The homogeneous kappa phase is illustrated by Fig. 10. It is quite resistant to etching reagents. The first effect of etching is to bring out the grain boundaries, which in these annealed alloys have a jagged outline. Upon prolonged etching a certain corrugated effect, which is particularly well brought out in polarized light, is obtained. Heavy and coarsely spaced striations appear, apparently Neumann bands, and there are apt to be two sets of parallel striations crossing at high angles and

causing some grains to assume a mosaic appearance as if the section were built up of parallelograms. The nature of these markings has not been determined, but they may possibly be due to incipient transition of kappa into alpha and gamma, somewhat similar to that in the beta brasses and bronzes explained by Greninger and Mooradian.¹¹

The microscopic distinction between alloys containing kappa and alpha and those containing homogeneous kappa is not in these alloys

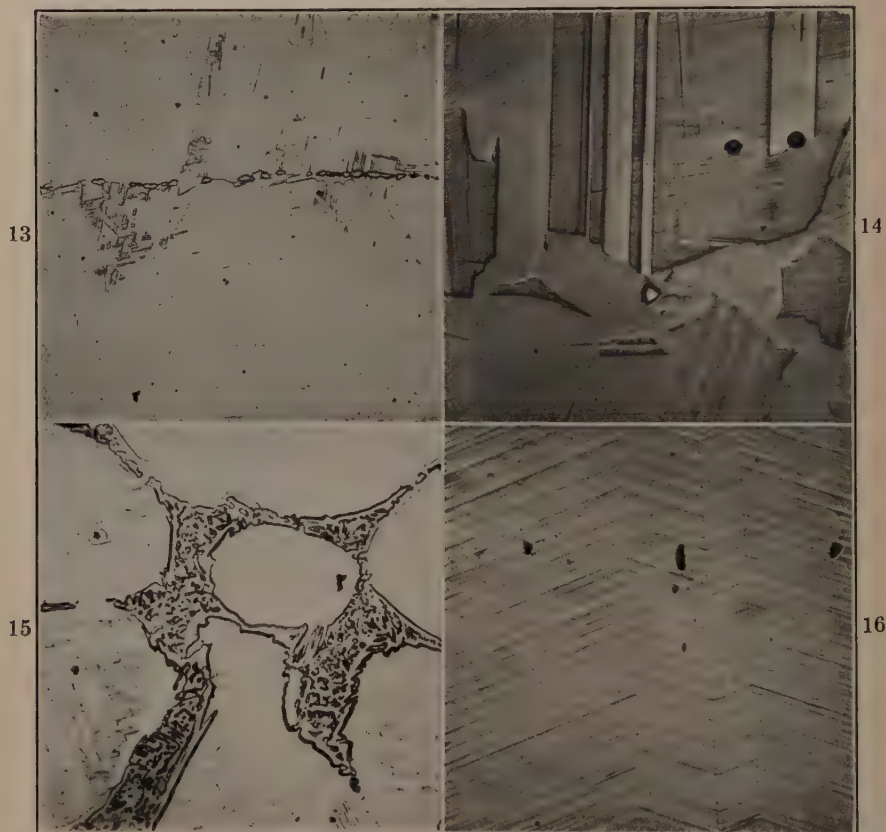


FIG. 13.—ALLOY No. 19. QUENCHED AFTER 72 HOURS AT 820° C. REHEATED TO 550° C. AND QUENCHED AFTER 96 HOURS. $\times 200$. ALPHA AND GAMMA.

FIG. 14.—ALLOY No. 61. QUENCHED AFTER 72 HOURS AT 512° C. OBLIQUE ILLUMINATION. $\times 200$. ALPHA AND GAMMA.

FIG. 15.—ALLOY No. 54. QUENCHED AFTER 18 HOURS AT 845° C. $\times 750$. ALPHA AND DELTA-KAPPA EUTECTOID.

FIG. 16.—ALLOY No. 66. QUENCHED AFTER 50 HOURS AT 825° C. REHEATED TO 560° C. AND QUENCHED AFTER 120 HOURS. $\times 200$. ALPHA, KAPPA AND GAMMA.

Chemical analysis in Table 1. Original magnifications given; reduced approximately $\frac{1}{3}$ in reproduction.

as clear as that obtainable by means of X-ray photograms. It seems not easy to distinguish the kappa phase shown in Fig. 10 from the kappa and alpha phase in Fig. 11. Neither is the distinction between the alpha

shown in Fig. 9 and the alpha plus kappa of Fig. 12 very clear. There is a tendency of the kappa phase when homogeneous to appear as equiaxed grains with few striations and markings. On the other hand, when kappa is intermixed with alpha it seldom is possible to tell which is alpha and which kappa. Nevertheless, it seems reasonable to assume that after standard cold-work and heat-treatment a satisfactory distinction by means of the microscope between alloys in these two-phase regions can be made.

Much more positive is the recognition of the gamma-phase alloys. Fig. 14 shows alpha with very small amounts of gamma. At 560° C. the conditions are as follows: Alloys 19 and 34, when containing small amounts of gamma as charged into the furnace at 560° C., still contain very small amounts of gamma after a three-day anneal. The same alloys were quenched from 820° C., so that they contained no gamma. After annealing at 560° C. for five days, the alloys thus pretreated may contain minute amounts of gamma. As the particles assumed possibly to be gamma here are extremely fine, there is doubt about the presence of gamma. We can conclude, however, that the first appearance of gamma cannot be placed above 560° C. or below 550° C. in these alloys.

The eutectoid obtained by quenching alloys from above 830° C. in the alpha + beta region is illustrated by Fig. 15. Alloys 54 and 58 at 832° C \pm 2° still show a few isolated patches of beta eutectoid, while at 820° C. no eutectoid was found. This would place the peritectic transition line at about 830° C.

DELINEATION OF THE PHASE BOUNDARIES

The alpha solid-solution boundary down to about 550° C. was determined mainly by X-ray methods. Results of phase identification as well as lattice parameter were used. Below 550° C. the lattice parameters were mainly relied upon although the microscopic work to some extent supported the X-ray work. The kappa boundary with the alpha and kappa region was determined exclusively by phase identification by X-ray photograms. The kappa, kappa + gamma boundary was determined jointly by X-ray photograms and microscopic work, mainly the latter. And finally, the eutectoid line was laid down at 557° C. after careful weighing of both X-ray photograms and micrographic evidence. There is a small amount of disagreement between microscopic results and X-ray results. The final diagram is the best representative compromise between the two.

ACKNOWLEDGMENTS

The initiation and progress of the present work is due Mr. W. H. Osborn, Director of the Research Department of the Phelps Dodge Corporation.

Mr. W. Upritchard and others of the Phelps Dodge Chemical Laboratory, under Dr. S. B. Tuwiner's direction, carried out the chemical analysis.

Preparation of samples and X-ray films was largely carried out by Mr. A. W. Kingsbury, who also ably assisted with other experimental work.

Dr. A. B. Kinzel and Mr. John S. Marsh read the original manuscript and advised as to its final form.

To all of these collaborators the author expresses his appreciation.

APPENDIX

An Appendix to this paper, giving chemical and spectrographic analyses, tables and description of apparatus, in 21 pages and 8 illustrations, has been issued through Auxiliary Publication and may be obtained from Bibliofilm Service, care U. S. Department of Agriculture Library, Washington, D. C., by ordering Document 1256, remitting 50¢ for copy in microfilm (read enlarged to full size on reading machines now widely available), or \$3.20 for copy in paper photoprints legible without mechanical aid.

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12. Appendix. See paragraph above.

DISCUSSION

(A. Allan Bates *presiding*)

C. S. SMITH,* Waterbury, Conn.—The essential agreement between Dr. Andersen's excellent work and my own, performed independently by different methods, is very gratifying. The points of disagreement are minor.

The thermal data given in Table 2 of my paper (p. 317), by which the kappa peritectoid point was fixed at 842°C., have been confirmed by additional annealing experiments. On heating, pure alloys contained all three phases, alpha, kappa, and beta, after annealing 2 hr. at 841.9°C., although less pure alloys (made from commercial silicon and melted in clay-graphite pots) had completely transformed to alpha + beta. On cooling from the alpha + beta range to 841.6°C., a somewhat similar case existed. One of the alloys had transformed completely (Fig. 17), others contained varying amounts of kappa and beta (Fig. 18). At 840°C. all but one impure alloy had transformed to alpha + kappa and that only contained a trace of beta. The true temperature of the peritectoid reaction, therefore, is above 841.6 and below 842°C. ($\pm 2.0^\circ\text{C}.$). Impurities depress this temperature.

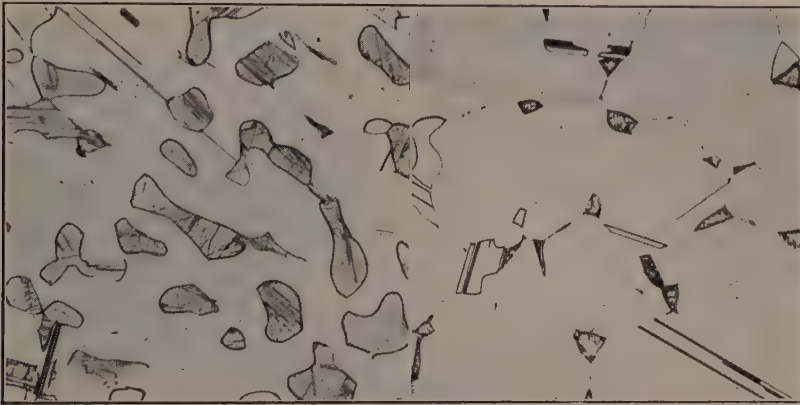


FIG. 17.

FIG. 18.

FIG. 17.—ALLOY 3461 (5.74 PER CENT SILICON) SLOWLY COOLED FROM 845° TO 841.6°C., HELD 2 HOURS AND QUENCHED. $\alpha + \kappa$.

FIG. 18.—ALLOY 3308 (5.35 PER CENT SILICON, 0.08 PER CENT IRON AND 0.02 PER CENT ALUMINUM), SAME TREATMENT AS FIG. 16. $\alpha + \beta$ (DECOMPOSED) + κ .

Both figures $\times 100$, alkaline peroxide etch.

Dr. Andersen's diagram, like Isawa's that was also based on X-ray work, shows a rather sharp increase of the alpha solubility near the peritectoid temperature. I have several microsamples showing that the maximum solubility at 842°C. is definitely not above 5.4 per cent and the 5.3 figure given in my paper still seems to be right. I humbly suggest that X-ray parameter measurements may possibly be in error as a result of partial transformation during cooling. Alpha is anisotropic under the polarizing microscope and is visibly covered with markings indicative of strain or twinning due to cooling stresses or incipient transformation. It is dangerous therefore to assume that the quenched samples represent at room temperatures the conditions existing prior to quenching. Under the microscope changes during quenching

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are readily detected and can be properly interpreted, but an X-ray diffraction line can tell nothing about the previous state of the lattice. The greatest divergence between our two determinations of the alpha boundary amounts to 0.45 atomic per cent Si, which is equivalent to a change of lattice constant of only 0.0003 \AA. , or 0.01 per cent. Is it safe to assume that no changes of this magnitude have occurred during quenching?

The idea of matching planes that I advanced to account for the banded alpha-kappa structures was sheer supposition unsupported by X-ray evidence. Dr. Andersen's statement that the X-ray reflections from the (220) planes in the alpha nearly coincide with the (110) reflections in the kappa phase seemed to be confirmation of this. The parameter measurements show, however, a lack of match amounting to about 0.05 per cent or 1 atom in 2000. Because I do not at present see any way of accounting for the microstructures that are observed if there is not an exact match of the juxtaposed planes—or at least a match as good as that normally existing within a grain of a single phase—I would like Dr. Andersen's opinion on three points:

1. Are the two reflections from the planes in question distinctly separable in a pattern of a single sample containing the two phases in equilibrium with each other?

2. Can the discrepancy be attributed to the differences in expansion coefficient of the two phases?

3. Is it possible that the juxtaposition of two lattices can strain them into a true match, possibly even by producing a stable composition gradient near the junction? If this were so, the parameter of a lattice of given composition would have to vary with the area and nature of its surface, but this does not seem utterly impossible.

It is not necessary to give controlled thermal and mechanical treatment to the specimens in order to render the microscopic detection of the kappa phase possible. The only requirement is a suitable etching reagent. A little experience with the alkaline peroxide etch will make identification of kappa positive under any conditions of distribution. On short etching the alpha remains lighter than the kappa while with prolonged etching it becomes darker.

A. G. H. ANDERSEN (author's reply).—The differences in the Smith diagram and my own may be accounted for by difference in the amount of impurities in the samples and different techniques. Since these alloys are not subject to rapid rates of transformations (except the β decomposition) it is improbable that the alpha phase has changed its composition with the amount of 0.45 atomic per cent Si in the fraction of a second elapsed during quenching. Any uncertainties in our determinations are not caused by such decomposition, and probably amount to about 0.2 atomic per cent. Our furnace temperatures were kept within 5°C. Using copper radiation and our precision camera, the coinciding lines in the two structures should actually be separated by about 0.2 mm., with a $\sin^2 \theta$ value of about 0.91. This distance is so small and the width of the lines so broad that they overlap without separation. The evidence for the difference in the spacing of the respective planes is based upon the accurate measurements of many lines in a large number of films of alloys from all over the three-phase regions concerned, and is conclusive.

Precipitation of one phase along certain crystallographic planes of another is, as Mehl has shown, not uncommon. The fact that structurally kappa can be derived from alpha with a minimum motion of the lattice points when the original alpha planes bear a simple relation to the newly formed kappa planes, limits the possible corresponding planes to either the (111) and (002) or the (220) and (110) planes in the alpha and kappa phase, respectively. Only on the former set is there a fairly good agreement in position and parameter. On both the (111) α and (002) κ the atoms lie at the apexes of equilateral triangles whose side is equal to $2 \times d(220)\alpha$ and $2 \times d(110)\kappa$ respectively. As can be seen from Fig. 19, these parameters do not coincide on any isotherm, but differ by 0.05 to 0.06 per cent for various temperatures. The inter-

planar spacings $(111)\alpha$ and $(002)\kappa$ differ by 0.025 per cent at the peritectoid to 0.08 per cent at the eutectoid temperature. The atomic radii of the alpha and kappa phases are identical in alloys quenched from the peritectoid temperature. At lower temperatures the radius of alpha progressively becomes smaller than that of kappa, with which it is in equilibrium until at the eutectoid temperature the difference is 0.034 per cent. It is unlikely that the expansion coefficients of the two phases involved vary in such a way as to account for the discrepancy.

If the two lattices should be elastically strained so that the respective single parameters of the atoms on the $(111)\alpha$ and $(002)\kappa$ become identical, compressive stresses along the $[001]$ direction in the kappa phase, and tensile stresses along a $[111]$ direction in the alpha phase could accomplish this. Thereby the alpha lattice would be

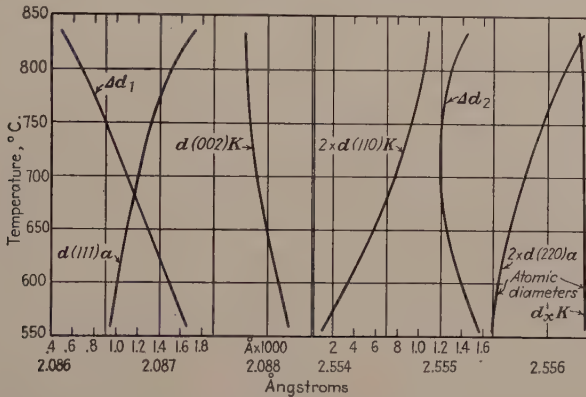


FIG. 19.—CORRESPONDING LATTICE SPACINGS AT COEXISTING ALPHA AND KAPPA PHASES AT VARIOUS TEMPERATURES.

(Prepared from phase compositions of alpha and kappa given in Fig. 1 and lattice spacings vs. compositions given in Figs. 4 and 5 (Appendix). Δd_1 at any temperature level is $d(002)\kappa - d(110)\alpha$ and Δd_2 is $2 \times d(220)\alpha - 2 \times d(110)\kappa$. The scale of the ordinate axis of Δd is 1000 times the scale of the lattice spacings proper, as indicated.)

distorted out of cubic symmetry. Calculations show that stresses of the order of 10,000 lb. per sq. in. would be needed, and would be associated with improbable variations in Poisson's ratio. Accordingly, the existence of strained lattices at the interfaces, while not impossible, is quite improbable.

Even if such conditions of strain do exist, the interface would be abrupt, a plane on either side of which the crystal symmetry and chemical composition would be distinctly different. The only thing to distinguish it from ordinary interfaces would be the gradual change from one lattice spacing to another on the direction perpendicular to the interface and the simultaneous gradual change in atomic packing and spacing on successive planes parallel to the interface. This would be sharply marked, but the regions about it would be quite different from usual regions around interfaces. Thermodynamically there would be no equilibrium, and such a condition should not be expected to prevail after anneals at above 600° or 700°C.

The Copper-rich Alloys of the Copper-nickel-phosphorus System

BY D. K. CRAMPTON,* H. L. BURGHOFF,† MEMBERS A.I.M.E., AND J. T. STACY‡

(New York Meeting, February 1940)

THE study of copper alloys of the age-hardening type has received considerable attention, and, among the alloys which the authors have considered, those containing small amounts of nickel and phosphorus as essential constituents seem especially interesting. Such alloys have attractively great capacity for being hardened and also have relatively high electrical and thermal conductivity in the hardened state. In addition, it has been found that the increase in hardness and strength imparted by aging can be greatly augmented by cold-working, so that excellent combinations of conductivity and strength are obtainable. In view of the possible importance of the alloys, it was considered desirable to investigate the solubility relationships in the copper-rich portion of the copper-nickel-phosphorus system. This paper presents some of the results obtained in this investigation to date and also gives properties of typical alloys that appear to be of commercial interest.

REVIEW OF LITERATURE

Copper-nickel System.—The binary copper-nickel system has long been known to consist of a series of simple solid solutions, copper and nickel being miscible at all temperatures and concentrations. This was established by Guertler and Tammann¹ in 1907 and confirmed by Tafel² in 1908.

Copper-phosphorus System.—The copper-phosphorus system has been studied by numerous investigators, so that the copper-rich portion is now definitely known. As most recently determined by Lindlief,³ this system has a eutectic at 8.38 per cent P, eutectic temperature being 714° C. Components of the eutectic are Cu_3P and alpha solid solution. Solid solubility of phosphorus in copper, according to Mertz and Mathewson,⁴ decreases from a maximum of about 1.75 per cent at 714° C. to about 0.6 per cent at 300° C.

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¹ References are at the end of the paper.

Capacity for age-hardening of copper-phosphorus alloys appears to be negligible in spite of the variable solubility of phosphorus in copper. Hanson, Archbutt and Ford⁵ found that the tensile strength of quenched strip in an alloy containing 0.95 per cent P was not changed by further heat-treatment, although Brinell hardness was increased from 43 to 52.

Nickel-phosphorus System.—Information concerning the nickel-phosphorus system appears to be meager. Konstantinov⁶ has reported a eutectic at 11 per cent P, eutectic temperature being 880° C. Three compounds are shown in his diagram: Ni_3P , dissociating at 975° C.; Ni_5P_2 , melting at 1184° C.; and Ni_2P , melting at 1112° C.

Copper-nickel-phosphorus System.—In 1925, Bamford⁷ noted that copper containing 1.52 per cent Ni, 0.12 per cent P and 0.05 per cent As increased in hardness after annealing. In 1928, Wise⁸ mentioned that copper-nickel-phosphorus alloys were age-hardenable, and later, through Merica,⁹ reported that the compound Ni_3P was the dispersion-hardening agent in such alloys. In 1935, Rollason and Bamford¹⁰ reported that a series of copper-nickel-phosphorus alloys, in which nickel ranged from 1.72 to 3.88 per cent and phosphorus from 0.03 to 0.50 per cent, were hardened by quenching and aging or by slow cooling. In 1939, Crampton and Burghoff¹¹ showed that both the ternary copper-nickel-phosphorus alloys and certain modifications thereof were characterized by very desirable combinations of conductivity and strength. None of these references discuss constitution or solubility relationships in any great detail.

EXPERIMENTAL WORK

Solidus and Alpha Solid Solubility

Alloys used for determination of the solidus surface and the alpha solid solubility and for demonstration of optimum ratio of nickel to phosphorus were made from electrolytic copper, electrolytic nickel, and 15 per cent phosphor-copper. The melts were prepared under charcoal in an Ajax-Northrup high-frequency furnace, "Norbide" crucibles being used, and were chill-cast in the form of rods $1\frac{1}{2}$ in. in diameter. Charges were 8 kg. in each case and nickel contents ranged from about 0.25 to 8 per cent and phosphorus contents from about 0.025 to 1 per cent. Alloys containing less than 0.1 per cent P were deoxidized with 0.02 per cent of 50-50 lithium-calcium alloy prior to addition of phosphor-copper, so that the phosphorus was free to alloy and did not have to function as deoxidizer. Analyses of the alloys are given in Table 1. The bars were cold-rolled and drawn, with suitable intermediate anneals, to 0.204-in. diameter, only a few alloys of the highest phosphorus contents not being capable of being so processed.

Melting points were determined by microscopic examination of specimens quenched in water after annealing for periods of 15 min.

Anneals were made at 20° C. intervals over the appropriate ranges, although no annealing was done above 1020° C. because of the limitations of the furnace employed. Temperature was automatically controlled to within about 5° C. of desired temperature. Three binary copper-phosphorus alloys were also studied in this part of the work, as the solidus curve given in the literature appeared to be uncertain.

TABLE 1.—*Analysis of Alloys*
REMAINDER IS COPPER IN EACH ALLOY

Alloy No.	Nickel, Wt. Per Cent	Phosphorus, Wt. Per Cent	Ni/P	Alloy No.	Nickel, Wt. Per Cent	Phosphorus, Wt. Per Cent	Ni/P
1	0.31	0.06	5.2	8	0.57	0.06	9.5
2	0.29	0.10	2.9	9	0.50	0.09	5.6
3	0.28	0.20	1.4	10	0.50	0.21	2.4
4	0.29	0.29	1.0	11	0.50	0.31	1.6
5	0.26	0.50	0.52	12	0.53	0.50	1.1
6	0.26	0.73	0.36	13	0.54	0.76	0.70
7	0.25	0.92	0.27	14	0.52	1.04	0.50
15	1.03	0.06	17.	21	2.07	0.06	35.
16	1.04	0.10	10.	22	2.08	0.10	21.
17	1.04	0.20	5.2	23	2.08	0.21	9.9
18	1.02	0.30	3.4	24	2.16	0.30	7.2
19	1.04	0.49	2.1	25	2.07	0.52	4.0
20	0.98	0.95	1.0	26	2.01	1.02	2.0
27	4.30	0.06	72.	32	8.04	0.05	160.
28	4.11	0.11	37.	33	8.00	0.10	80.
29	3.96	0.20	20.	34	7.80	0.32	24.
30	4.22	0.30	14.				
31	4.56	0.50	9.1				
35	0.89	0.09	9.9	41	0.18	0.05	3.6
36	0.78	0.20	3.9	42	0.11	0.11	1.0
37	0.68	0.31	2.2	43	0.056	0.15	0.37
38	0.80	0.17	4.7	44	0.49	0.027	18.
39	0.86	0.14	6.1	45	0.12	0.29	0.41
40	0.88	0.12	7.3				
46		0.42					
47		0.76					
48		1.18					

Samples for determination of the alpha-phase boundary by microscopic examination were annealed as above in groups, protected by powdered charcoal to avoid excessive surface oxidation, at 900° C. for 24 hr. One group was then quenched in water for examination after this treatment. The remaining samples were allowed to furnace-cool to

800° C., another group being quenched after having been at this temperature for 24 hr. This procedure was continued for temperatures of 700°, 600°, and 500° C. As it was definitely known that the system was one of decreasing solubility with decreasing temperature, it could be expected

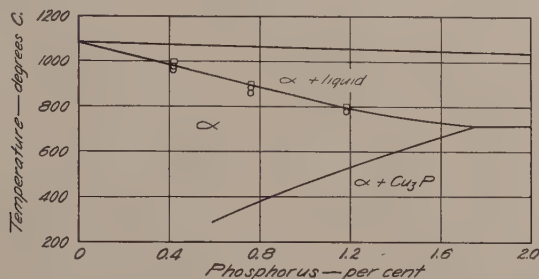


FIG. 1.—EQUILIBRIUM RELATIONS IN COPPER-RICH COPPER-PHOSPHORUS ALLOYS.

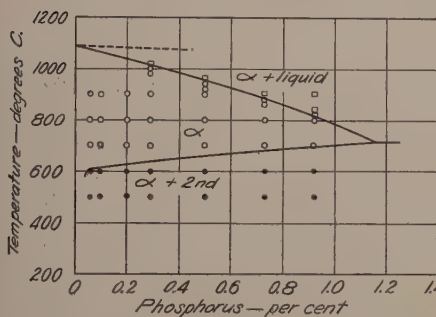


FIG. 2.

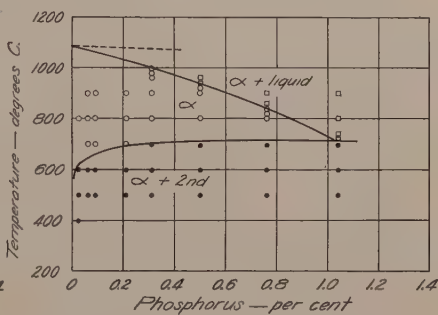


FIG. 3.

FIG. 2.—COPPER-NICKEL-PHOSPHORUS SECTION AT 0.25 PER CENT NICKEL.

FIG. 3.—COPPER-NICKEL-PHOSPHORUS SECTION AT 0.5 PER CENT NICKEL.

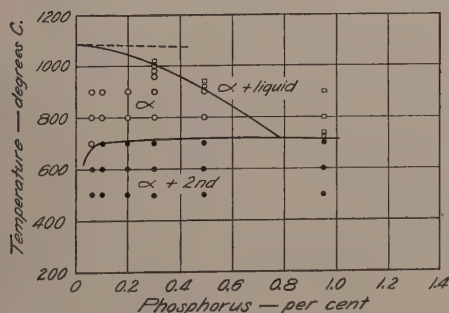


FIG. 4.

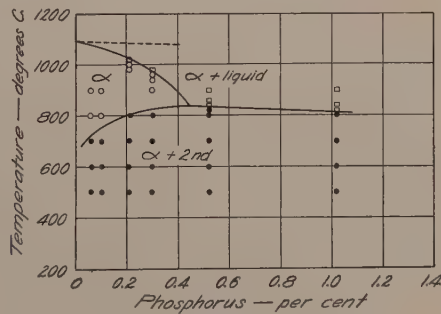


FIG. 5.

FIG. 4.—COPPER-NICKEL-PHOSPHORUS SECTION AT 1 PER CENT NICKEL.

FIG. 5.—COPPER-NICKEL-PHOSPHORUS SECTION AT 2 PER CENT NICKEL.

logically that examination of the various microstructures after these treatments would show the presence or absence of a second phase and therefore locate the alpha solid-solubility boundary at relatively high temperatures.

Location of the alpha boundary at some of these temperatures and at 400° and 300° C. was also accomplished by electrical conductivity deter-

minations. For this part of the investigation a suitable sample of each alloy was annealed for 24 hr. at 900° C. or some slightly lower temperature in the alpha field, quenched in water, and thereafter reheated for periods of 24 hr. followed by quenching at each of the temperatures:

700°, 600°, 500°, 400°, and 300° C. Reheating and quenching was done at successively lower temperatures and conductivity for each condition was determined. As the structure at high temperature had previously been determined by microscopic examination, any increase in conductivity due to reheating or aging a specimen originally containing only alpha indicates the appearance of a second phase. Attainment of complete equilibrium in the formation of the second phase would not be necessary in this procedure. Anneals for this group of tests were made in a furnace automatically controlled to within about 2½° C., and a reducing atmosphere was

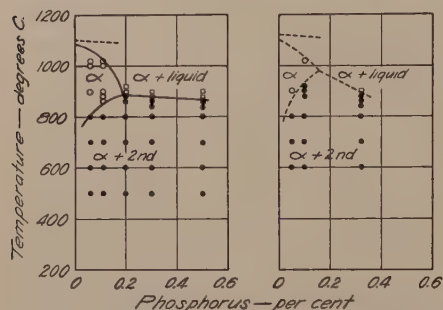


FIG. 6.—COPPER-NICKEL-PHOSPHORUS SECTIONS AT 4 AND 8 PER CENT NICKEL.

employed at 700° C. and higher. Electrical conductivity was determined by means of a Hoopes' bridge and specimens were reversed in the bridge to obtain duplicate readings.

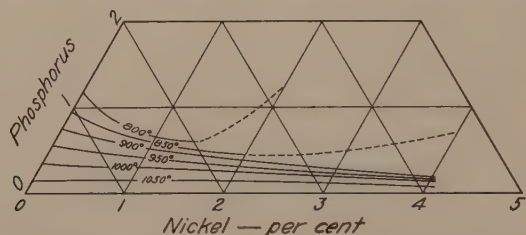


FIG. 7.—ISOTHERMS ON COPPER-NICKEL-PHOSPHORUS SOLIDUS SURFACE.

employed at 700° C. and higher. Electrical conductivity was determined by means of a Hoopes' bridge and specimens were reversed in the bridge to obtain duplicate readings.

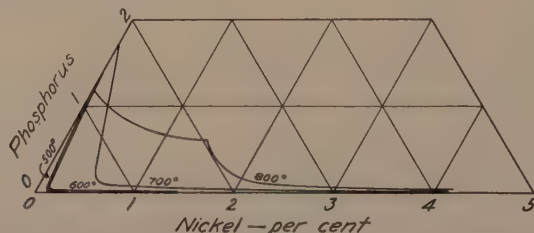


FIG. 8.—ALPHA SOLID SOLUBILITY LIMITS AT VARIOUS TEMPERATURES.

Results of melting-point and solid-solubility determinations are shown in Figs. 1 to 6, which are partial sections through the ternary diagram at 0 per cent and approximately 0.25, 0.5, 1, 2, 4 and 8 per cent

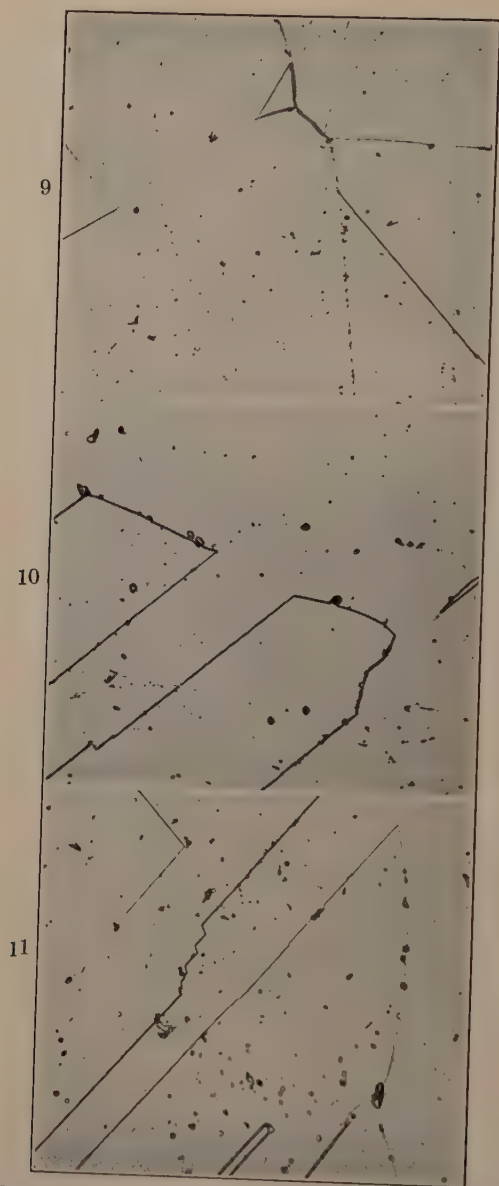
Ni. In the ternary alloys the three-phase field of equilibrium among alpha, the second solid phase, and liquid, which would be expected between the fields alpha plus liquid and alpha plus second solid phase was not observed and is probably of limited extent in the concentrations here investigated although this region was not examined critically. The contours of the solidus surface are indicated by the isotherms of Fig. 7, and Fig. 8 shows the alpha-phase boundary at 800°, 700°, 600° and 500° C. In the latter figure the values for binary copper-phosphorus alloys were taken from Mertz and Mathewson's work. In addition to the alloys shown in the quasibinary sections, several others were of assistance in delineating the boundaries given in Fig. 8. The compositions of these alloys and their structures are listed in Table 2.

TABLE 2.—*Compositions of Miscellaneous Alloys and Their Structures at Various Temperatures*

Alloy No.	Analysis, Per Cent		Structure at				
	Nickel	Phosphorus	800° C.	600° C.	500° C.	400° C.	300° C.
41	0.18	0.05	α	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$
42	0.11	0.11	α	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$
43	0.056	0.15	α	α	α	α	α
45	0.12	0.29	α	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$	$\alpha + 2nd$

As shown in the sections of constant nickel content, the maximum solubility of phosphorus decreases markedly as nickel content increases, approximate values being 1.75, 1.15, 1.0, 0.8, 0.45, 0.2, and 0.15 per cent for 0, 0.25, 0.5, 1, 2, 4, and 8 per cent Ni, respectively. The relations in alloys containing 8 per cent Ni are very indefinite because of the few data obtained on such alloys. The temperature of maximum solid solubility appears to vary but little from the value of 714° C. for 0 per cent Ni up to 1 per cent Ni, then increases sharply to about 825° C. at 2 per cent Ni, and increases regularly with nickel content thereafter. An understanding of the true significance of this apparent sharp rise between 1 and 2 per cent would probably require greater precision and detail than were used in this investigation.

The solubility of nickel and phosphorus decreases sharply at lower temperatures, especially for compositions in which the nickel is considerably in excess of the phosphorus. In alloys containing only 0.25 per cent Ni, the solubility of phosphorus decreases from about 1.0 per cent at 700° C. to less than 0.05 per cent at 600° C., and in alloys containing 0.5 per cent Ni the solubility of phosphorus at 600° C. is definitely less than 0.027 per cent. For example, an alloy containing 0.49 per cent Ni and 0.027 per cent P had a conductivity value of 61.75 per cent International Annealed Copper Standard as quenched from 800° C.



FIGS. 9-11.—ALLOYS CONTAINING NICKEL AND PHOSPHORUS, SUCCESSIVELY ANNEALED AT TEMPERATURES LISTED, AND QUENCHED.

Fig. 9. Ni, 0.57 per cent; P, 0.06.
900°, 800°, 700°, 600° and 500° C.

Fig. 10. Ni, 1.03 per cent; P, 0.06.
900°, 800°, 700° and 600° C.

Fig. 11. Ni, 2.07 per cent; P, 0.06.
900°, 800° and 700° C.

Etch: ammonia and peroxide. $\times 250$.

and 68.50 per cent I.A.C.S. as subsequently reheated for 24 hr. at 600° C. and quenched. Solubility of such alloys is still less at lower temperatures, as shown by further increases in conductivity for annealing temperatures down to 300° C.

Microstructure

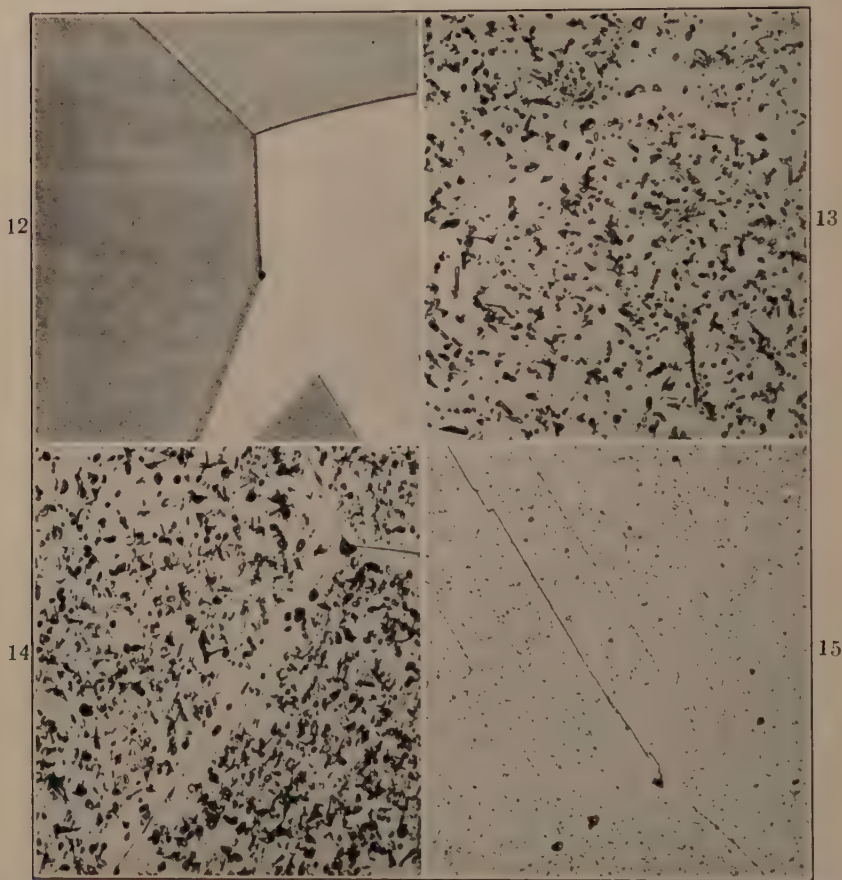
The phase precipitated from the alpha solution was visible in all but the most dilute alloys. Microstructures typical of alloys containing 0.06 per cent P and approximately 0.5, 1 and 2 per cent Ni, respectively, are shown in Figs. 9, 10 and 11, in which the particles of second phase can be distinguished. The precipitation is more readily followed in an alloy containing 1.04 per cent Ni and 0.49 per cent P, as shown in Figs. 12 to 15, which illustrate the microstructure as annealed successively for 24 hr. at 900° C., 700°, 600°, and 500° C., and quenched; an intermediate step for 800° C. is not shown. This alloy consists only of alpha solution as quenched from both 900° and 800° C., but contains a second phase as subsequently quenched from 700° C. and successively lower temperatures. The nature of this precipitate is seen to vary between 600° and 500° C., for, as developed at 500° C., the particles are much finer and more widely dispersed than at 600° C. A transformation is thus indicated between these two temperatures. If this were not so, the particles of the second phase developed at 600° C. would not be expected to decrease in size at 500° C., although additional precipitation would undoubtedly occur. This difference in structure as successively annealed at 600° and 500° C. appeared to be generally characteristic of the other alloys studied. Actual age-hardening of the copper-nickel-phosphorus alloys is best accomplished well below 600° C., so that the precipitation in the aging process corresponds to that shown for the treatment at 500° C. When such alloys are aged to produce commercially attractive properties, as will be discussed later, the precipitate cannot be resolved under the microscope.

Optimum Nickel-phosphorus Ratio

Examination of the alpha boundary at various temperatures shows that, for a given nickel plus phosphorus content, the solubility is least for alloys in which the nickel is considerably in excess of the phosphorus. This is as might be expected if one assumes that the precipitate is one of the known compounds of nickel and phosphorus.

In order to determine the ratio of nickel to phosphorus considered optimum with regard to increase in strength and conductivity due to precipitation or aging treatment, a series of alloys containing 99 per cent Cu and 1 per cent Ni + P, with the ratio of nickel to phosphorus varying widely, was tested. Electrical conductivity and tensile strength of these alloys were determined after annealing 24 hr. at 800° C. and quenching,

and after subsequently reheating or aging at 450° C. for 24 hr. The tensile strength and conductivity results are plotted in Fig. 16 as functions of ratio of nickel to phosphorus. Each curve passes through a rather flat maximum range but apparently not at exactly the same value



FIGS. 12-15.—ALLOYS CONTAINING 1.04 PER CENT NICKEL, 0.49 PHOSPHORUS, 98.47 COPPER (BY DIFFERENCE).

Fig. 12. As annealed 24 hours at 900° C. and quenched.

Fig. 13. As successively annealed 24 hours at 900°, 800° and 700° C. and quenched.

Fig. 14. As successively annealed 24 hours at 900°, 800°, 700° and 600° C. and quenched.

Fig. 15. As successively annealed 24 hours at 900°, 800°, 700°, 600° and 500° C. and quenched.

Etch, ammonia and peroxide. $\times 250$.

of Ni/P. There is a sharp break in the tensile-strength curve at Ni/P = 4, which was not expected, but this was checked very closely in a duplicate set of treatments upon additional samples of these alloys. The maximum points are nearer to the value 4.73, required by the compound Ni_5P_2 , than to 3.78 or 5.68, required by Ni_2P and Ni_3P , respec-

tively. Lacking specific investigation of the precipitating phase, it may therefore be postulated that Ni_5P_2 , under these conditions of heat-treatment, is the precipitating phase, although the data are by no means sufficiently conclusive to eliminate consideration of Ni_3P , suggested by Wise to be the hardening phase in copper-nickel-phosphorus alloys.

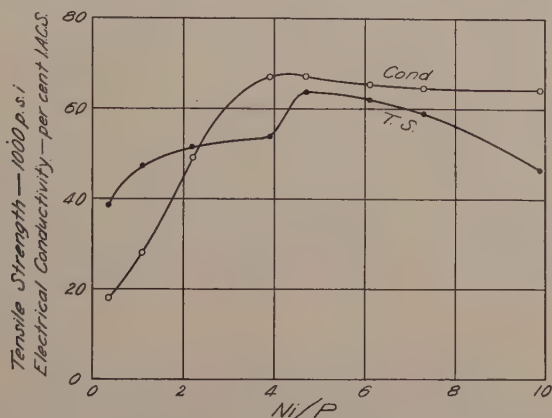


FIG. 16.—EFFECT OF NICKEL-PHOSPHORUS RATIO UPON STRENGTH AND CONDUCTIVITY OF ALLOYS CONTAINING 1 PER CENT NICKEL PLUS PHOSPHORUS, AS QUENCHED FROM 800°C . AND AGED 24 HOURS AT 450°C .

Additional data concerning best proportions of nickel and phosphorus are presented in Fig. 17, which shows conductivity as a function of Ni/P for alloys of various contents of nickel after having been finally annealed 24 hr. at 400°C . and quenched, following similar treatments at 900° ,

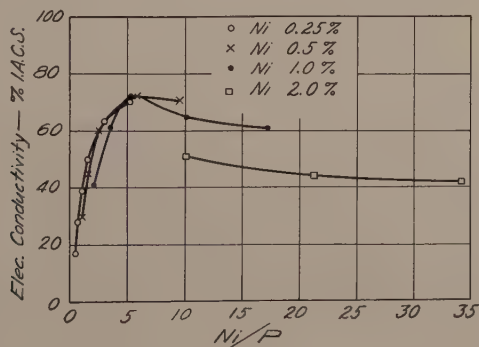


FIG. 17.—EFFECT OF NICKEL-PHOSPHORUS RATIO UPON CONDUCTIVITY OF ALLOYS WITH VARIOUS CONSTANT NICKEL CONTENTS AS ANNEALED 24 HOURS AT EACH OF THE TEMPERATURES 900° , 700° , 600° , 500° AND 400°C ., SUCCESSIVELY, AND QUENCHED.

700° , 600° and 500°C . Although all the curves shown do not pass through a point of maximum conductivity, it appears that such maximum point occurs at a value of Ni/P approximately equal to 5.

Regardless of the exact composition of the precipitating phase, it is apparent that optimum combination of strength and conductivity

in the quenched and aged condition is obtained for this proportion of nickel and phosphorus. Although the exact ratio is not very critical, wide departures are not desirable as conductivity is greatly lowered by an excess of phosphorus while an excess of either nickel or phosphorus results in material decrease of attainable strength.

Properties of Alloys of about 5 to 1 Nickel to Phosphorus Weight Ratio

Effect of Increasing Nickel plus Phosphorus.—A series of five alloys of compositions as shown in Table 3 were cast in chill molds in rods $1\frac{1}{2}$ in. in diameter and worked down by the normal mill procedure to 0.204-in. diameter. On this size they were all annealed for one hour at 730° C. and water-quenched. Each was divided into three portions; one portion was not aged, a second portion was aged 4 hr. at 425° C., and the third portion similarly aged and subsequently cold-drawn 84 per cent.

TABLE 3.—*Effect of Increasing Nickel plus Phosphorus*

Alloy No.	Nickel, Per Cent	Phosphorus, Per Cent	Ni + P, Per Cent	Ratio Ni:P
49 ^a				
50	0.51	0.09	0.60	5.6
51	1.00	0.19	1.19	5.3
52	1.48	0.28	1.76	5.3
53	1.81	0.35	2.16	5.2

^a Tough-pitch copper (99.90 + copper).

The results of tests on all the wires are shown in Fig. 18, where tensile strength and conductivity are plotted as functions of nickel plus phosphorus content. The effect of nickel plus phosphorus on tensile strength in the soft condition is seen to be rather slight. In the aged condition a much greater increase of strength results from the addition of nickel plus phosphorus, and when aged and subsequently cold-drawn to a total reduction of 84 per cent, the increase in strength with alloy content is even more marked. Both as aged and as aged and drawn, the major part of the increase is found for a total alloy addition of about 1.25 to 1.5 per cent, a relatively small increase resulting from further alloy addition.

The conductivity curves for all three conditions are of similar form, showing a marked decrease in conductivity with initial additions of nickel plus phosphorus, and progressively less effect with increasing alloy content. For any composition there is a relatively great increase in conductivity due to aging after the solution treatment and then a slight drop on application of subsequent cold-work. The total effect of alloying, heat-treatment and cold-working is to produce very attractive

combinations of tensile strength and conductivity in alloys containing about 1.25 per cent or more of nickel plus phosphorus.

Effect of Solution, Aging, and Mechanical Treatments.—The effect of time and temperature of aging on properties exhibited were investigated,

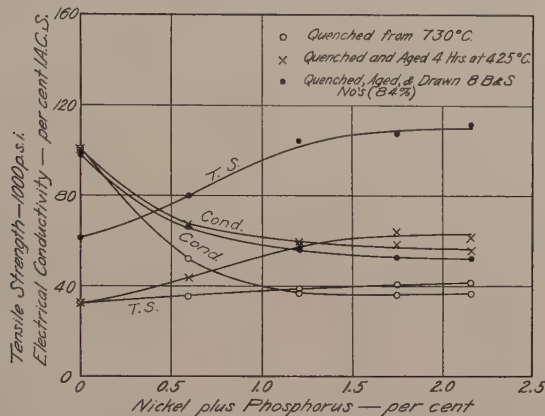


FIG. 18.—EFFECT OF NICKEL PLUS PHOSPHORUS CONTENT UPON STRENGTH AND CONDUCTIVITY. NICKEL-PHOSPHORUS RATIO APPROXIMATELY 5:1.

using a single coil of wire of alloy No. 17 listed in Table 1, containing: copper, 98.76 per cent; nickel, 1.04; phosphorus, 0.20; Ni/P, 5.2. The whole coil of wire drawn by the usual procedure to 0.204 in. was annealed

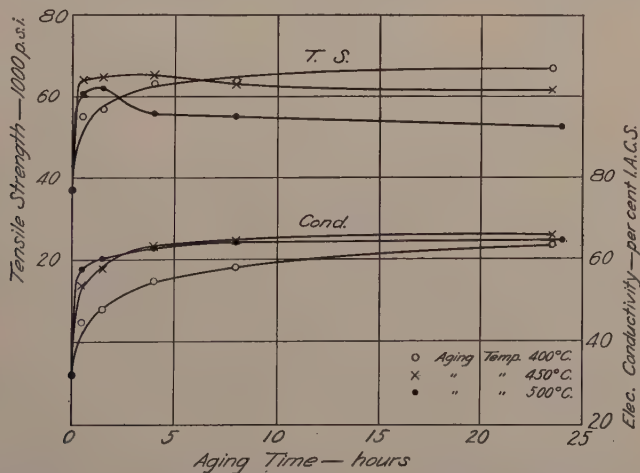


FIG. 19.—EFFECT OF AGING TEMPERATURE AND AGING TIME UPON STRENGTH AND CONDUCTIVITY OF WIRE PREVIOUSLY QUENCHED FROM 800° C. 1.04 per cent Ni, 0.20 P.

at 800° C. and water-quenched. Portions were then cut from the coil and aged for periods of $\frac{1}{2}$, $1\frac{1}{2}$, 4, 8 and 24 hr. at each of the temperatures 400°, 450°, and 500° C. Tests were then made of tensile strength and electrical conductivity, these being shown graphically in Fig. 19.

After the solution treatment and prior to aging, the wire had a tensile strength of 37,100 lb. per sq. in., and a conductivity of 31.9 per cent I.A.C.S. On aging at 400° C., both properties improve rapidly with short aging time and then continue to improve at progressively lesser rates as the time is increased.

Using an aging temperature of 450° C., both strength and conductivity increase more rapidly than at 400° C. There is a well-defined although not sharp maximum in the strength curve at about 2 to 3 hr., a slight overaging being apparent after longer annealing. The conductivity, as would be expected, however, increases continuously with time.

At 500° C., there is a distinct maximum in the strength curve at 1 to 1½ hr. and a rather sharp drop between 2 and 4 hr. Again the conductivity curve rises continuously up to 24 hours.

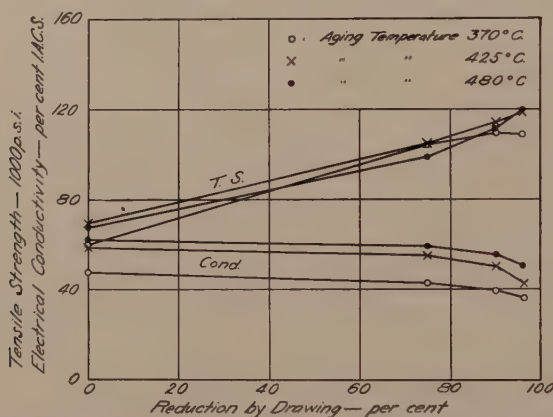


FIG. 20.—EFFECT OF AGING TEMPERATURE AND DEGREE OF COLD-WORK ON STRENGTH AND CONDUCTIVITY OF MATERIAL PREVIOUSLY QUENCHED FROM 790° C.
98.56 Cu, 1.18 Ni, 0.23 P.

The effect of aging temperature and degree of cold-work on strength and conductivity of wires of a ternary alloy containing copper 98.56 per cent, nickel 1.18 per cent and phosphorus 0.23 per cent is shown in Fig. 20. These data resulted from tests made on wire initially 0.204-in. diameter, quenched from 790° C., aged for 4 hr. at the temperatures indicated and subsequently drawn varying amounts up to 96 per cent reduction of area.

The strength increases with the percentage of reduction by drawing for each of the different aging temperatures used. The optimum aging temperature apparently is at about 425° C., a temperature of 480° C. showing slight but distinct overaging effects. Variation of aging temperature has a relatively greater effect on electrical properties, the conductivity for any degree of reduction increasing considerably with increased aging temperature at the constant time used. Presumably this indicates more complete precipitation at higher temperatures, as increased con-

ductivity is largely a function of degree of precipitation rather than one of size or distribution of particles of the precipitated phase.

The data shown in Fig. 21 indicate the effect of variation in quenching treatment on the same alloy and size of wire shown for Fig. 20. All wires were quenched at temperatures of 705°, 790° and 870° C., after which they were aged 4 hr. at 425° C. and drawn as indicated. It is seen that

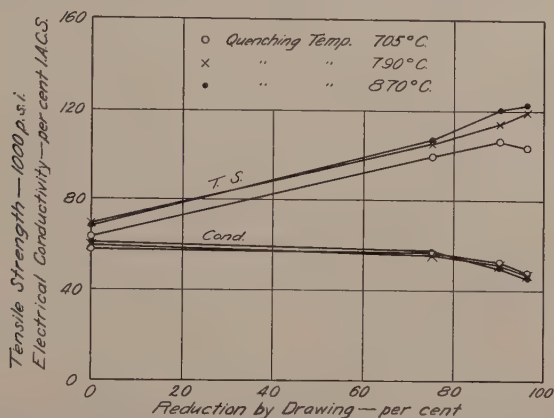


FIG. 21.—EFFECT OF QUENCHING TEMPERATURE ON STRENGTH AND CONDUCTIVITY OF MATERIAL SUBSEQUENTLY AGED 4 HOURS AT 425° C. AND COLD-DRAWN.
98.56 Cu, 1.18 Ni, 0.23 P.

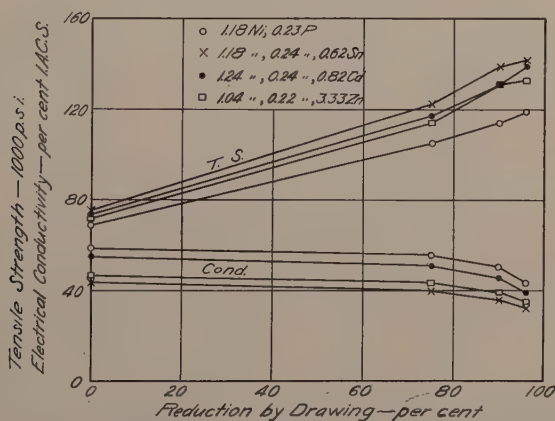


FIG. 22.—EFFECT OF ADDITION OF TIN, CADMIUM AND ZINC UPON STRENGTH AND CONDUCTIVITY OF WIRE QUENCHED FROM 790° C., AGED 4 HOURS AT 425° C. AND COLD-DRAWN.

quenching temperatures of 790° and 870° C. give somewhat greater final strengths than does a temperature of 705° C. The variation in quenching temperature, however, has only a slight effect on conductivity.

From the data in Figs. 20 and 21 it may be concluded that for maximum strength the alloy should be given a solution treatment at 790° to 870° C. and aged at about 425° C. For maximum conductivity the

quenching temperature is not critical, but the aging should be at about 480° C. For a good combination of strength and conductivity a quench from about 790° C. and aging treatment between 425° and 480° C. is indicated.

Effect of Added Alloying Elements.—The addition of small amounts of tin, cadmium, or zinc to the basic copper-nickel-phosphorus alloy affects the strength and conductivity as shown in Figs. 22 and 23. The material used to obtain these data was wire fabricated from bars cast 1½ in. in diameter in chill molds. All materials were worked down by normal mill procedure to 0.204-in. diameter, were then annealed at 790° C. and quenched, aged 4 hr. at 425° C. and finally drawn varying reductions up

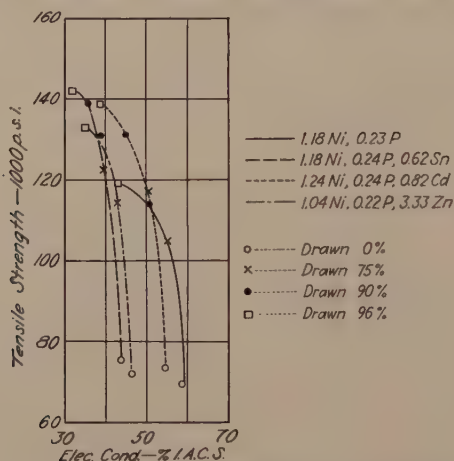


FIG. 23.—TENSILE STRENGTH VERSUS CONDUCTIVITY.

to 96 per cent. The actual compositions of the four alloys used were as follows, the balance in each instance being copper:

Alloy No.	Nickel, Per Cent	Phosphorus, Per Cent	Added Element, Per Cent
54	1.18	0.23	
55	1.18	0.24	0.62 tin
56	1.24	0.24	0.82 cadmium
57	1.04	0.22	3.33 zinc

It is seen that the strength is an increasing and the conductivity a decreasing function of the reduction by drawing. Also, the individual fourth elements added increase the strength but simultaneously decrease the conductivity. It seems probable that these effects are largely explained by assuming these added elements to be present in solid solution in the matrix.

In any such series of alloys or treatments where strength and conductivity are both affected, the combined properties are not too well

shown by curves plotted as in Fig. 22. It has been found that an excellent method of indicating such effects is that shown in Fig. 23, where the same data are used to plot strength as a function of the conductivity for each of the various treatments. In the resulting family of curves, the one showing the better combination of strength and conductivity is located farthest from the origin. Fig. 23 indicates that for lower degrees of cold-drawing the straight ternary alloy is superior to any of the quaternary ones, but that for higher reductions the reverse is true. The cadmium-bearing alloy, particularly, shows an outstanding combination of properties for reductions of 75 per cent and upward.

The effect of certain combinations of the solution, aging and drawing treatments on the properties of the cadmium-bearing alloy No. 56 are

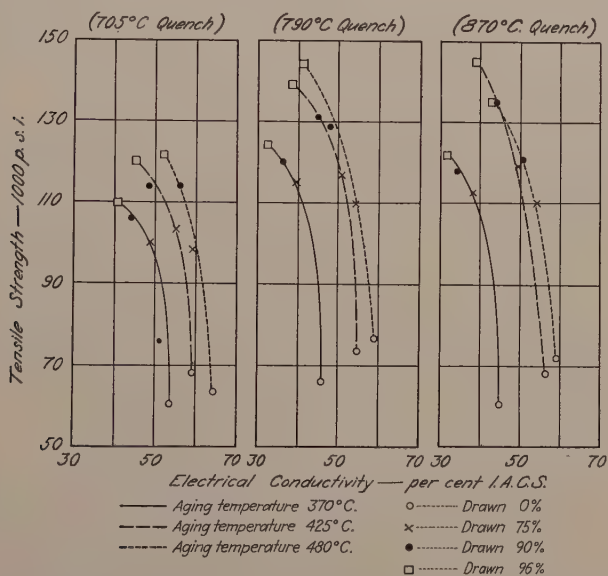


FIG. 24.—TENSILE STRENGTH VS. CONDUCTIVITY FOR WIRES AGED 4 HOURS AND COLD-DRAWN 0 TO 96 PER CENT AFTER HAVING BEEN QUENCHED FROM 705°, 790° AND 870° C., RESPECTIVELY.

97.69 per cent Cu, 1.24 Ni, 0.24 P, 0.82 Cd.

shown in Fig. 24. The wire after drawing to 0.204-in. gauge was subjected to solution treatments at temperatures of 705°, 790° and 870° C., followed in each instance by aging for 4 hr. at temperatures of 370°, 425° and 480° C. Finally, all wires were cold-drawn 0, 6, 10 and 14 B. and S. numbers hard.

The results of this series of tests are plotted in the same manner as described for Fig. 23, this procedure showing clearly the relative merits of the different treatments as determining the combined tensile and conductivity properties. It is seen that the 705° C. solution treatment yields lower strength but higher conductivity than either of the two

higher-temperature solution treatments. However, for each of the solution treatments, an increase in aging temperatures always gives better combinations of strength and conductivity.

Complete data on the effect of all possible combinations of solution, aging, and cold-working treatments are not given in the present paper. It should be noted that the data presented are illustrative rather than comprehensive, and other modifications of exact composition and treatment are capable of yielding a wide range of properties, some perhaps better than any indicated here.

SUMMARY

The solidus surface and limits of alpha solid solubility were determined for copper-nickel-phosphorus alloys containing up to 8 per cent Ni and 1 per cent P. Solubility of nickel and phosphorus decreased markedly with decreasing temperatures, as little as 0.2 per cent Ni + P forming a second phase at 500° C. when present in suitable proportions. Because of this low solubility, attractive combinations of conductivity and strength were shown to be obtainable in quenched and aged alloys. Best properties were found to be obtained in alloys in which ratio of nickel to phosphorus was about 5 to 1. The exact nature of the precipitating phase was not established in the investigation, but it appeared that the phase precipitated in the age-hardening range of temperatures, at and below about 500° C., was different from the phase precipitated at somewhat higher temperatures.

Investigation of the properties of alloys containing nickel and phosphorus in the ratio of about 5 to 1 showed that the most useful hardenability is attained in alloys containing about 1.25 to 1.5 per cent Ni + P and that hardness or strength attainable by age-hardening increases only gradually for higher alloy contents. Electrical conductivity of about 67 per cent I.A.C.S. and tensile strength of about 65,000 lb. per sq. in. were realized in alloys containing about 1 per cent Ni + P in the desired ratio. Such alloys were found to be capable of extensive cold-working after age-hardening, so that the strength could be still further increased. Addition of alloying elements such as tin, cadmium and zinc yielded slightly modified but also attractive properties, strength being increased while conductivity was somewhat decreased.

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DISCUSSION

(J. L. Christie presiding)

W. C. ELLIS,* New York, N. Y.—New alloys such as those described by Crampton, Burghoff and Stacy, combining high strength and high conductivity, are additions to the metal family that are particularly welcomed by the electrical industry. Alloys of this type find wide application as electrical conductors where a higher strength is required than that of hard-drawn copper. Each gain in conductivity in equivalent size of wire translates into a lowered transmission loss. Likewise, higher strengths increase the life of conductors in that greater resistance is offered to failure due to ice loads or incidental hazards, and advantage can sometimes be taken of both higher strength and conductivity to reduce the size of wire used and obtain the same performance with consequent economies.

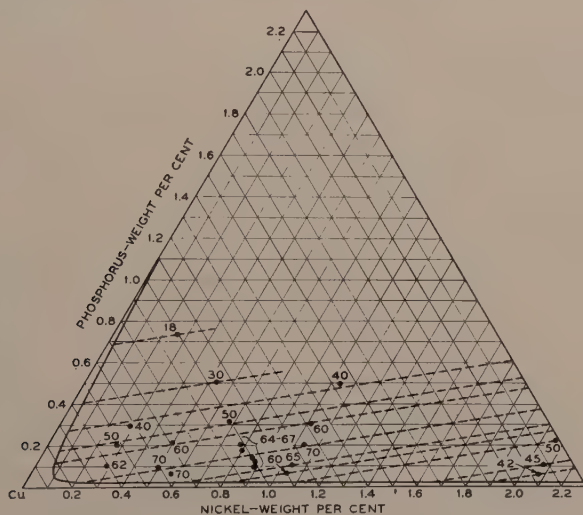


FIG. 25.—REPRESENTATION OF CONDUCTIVITY VALUES OF COPPER-NICKEL-PHOSPHORUS ALLOYS ON THE TERNARY COMPOSITION PLOT FOR APPROXIMATE EQUILIBRIUM AT 400° TO 500°C.

If the alloy compositions are plotted on a ternary diagram with notations of the values of the electrical conductivity in the condition approaching equilibrium at about 400° to 500°C., as given in the authors' paper, a consistent pattern is obtained as shown in Fig. 25. The general picture is that with increasing phosphorus contents the conductivity decreases and the same trend occurs to a lesser extent with increasing nickel contents. If one were to draw in speculative tie lines originating from the region of the phosphide compounds in the binary system nickel-phosphorus, as is done in Fig. 25, the conductivities of the several alloys plotted are in line with those expected for the terminal solid solutions as predicted from the conductivities in the two binary systems copper-phosphorus and copper-nickel involved. I want to emphasize that this analysis is highly speculative in view of lack of information concerning the conductivities of the ternary solid solution compositions, and concerning the structure

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in general in the ternary regions. No conclusion as to the identity of the phase in equilibrium with the alpha can be drawn because all of the alloys are close to the copper corner. Moreover, both phases contribute to the electrical conductivity.

J. L. CHRISTIE,* Bridgeport, Conn.—Are the brass mills yet in a position to consider production on a commercial scale of alloys that involve quenching from 800°C. followed by low-temperature annealing for times up to 8 hours?

E. M. WISE,† Bayonne, N. J.—The authors are to be congratulated on their work on these interesting alloys, and in particular for presenting data on mechanical and electrical properties along with those on the equilibria. In too many of our papers data are presented on equilibria only, which leaves the possible useful properties open to conjecture.

It would appear that applications of the present alloys fit into the field of hardened coppers where strengths in excess of those provided by cadmium copper are required. The nickel-phosphorus alloys also may have other advantages, particularly in leaded alloys where some of the other age-hardening combinations are not applicable. Likewise, nickel plus phosphorus may be helpful where an increase in annealing temperature or a reasonable creep strength is required.

The effectiveness of cold-work applied to alloys containing dispersed particles—even quite coarse dispersions—has long been utilized in producing very strong steel wire and apparently is involved in strengthening some of the cold-worked aluminum alloys containing small amounts of nickel, chromium and manganese, with or without magnesium silicide, but with this exception does not appear to have been extensively used with nonferrous alloys.

It is important to be aware of the effect of other elements, phosphorus in particular, upon the properties of the low-nickel-content copper alloys, as the combination of nickel plus phosphorus or silicon is necessary to develop the properties that are sometimes reported, and which would not be shown by a simple low-nickel copper alloy.

To complete the history, it may be recorded that my first work on the copper-rich phosphorus-nickel alloys was done on April 1 to 6, 1925, at the Wadsworth Watch Case Co., Dayton, Ky., and was an outgrowth of work started in 1923 on the copper-rich nickel-silicon alloys. In 1925 it was observed that copper containing 2.12 per cent Ni and about 0.3 per cent P hardened on aging as low as 300°C., and a similar alloy showed reasonable hardening on furnace cooling. The following year complete aging curves on these alloys showed that alloys quenched from 800°C. reached maximum hardness (for 30 min. aging) at 500°C.

H. L. BURGHOFF (authors' reply).—The observed conductivity of a particular ternary alloy, heat-treated to equilibrium or some intermediate condition at a given temperature, may be referred to that of another ternary alloy of equal conductivity, containing the alpha phase only. It is more accurate if the composition of the precipitating phase is known, and less accurate if this is not known, so that one must guess at the ratio of alloying elements in the terminal solid solution or equivalent ternary alloy.

A heat-treated copper-nickel-phosphorus alloy has been brought into the freely machinable class of alloys by the addition of tellurium, and is commercially established. This fact is pertinent to both Mr. Wise's and Mr. Christie's remarks. With particular reference to Mr. Christie's question, the alloy is fully heat-treated although the aging time is less than 8 hr. However, another copper alloy, requiring solution treatment and quenching at well above 800°C. and subsequent aging for about 8 hr., has been in regular commercial production for several years.

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The Cobalt-nickel-silicon System between 0 and 20 Per Cent Silicon

BY ARTHUR C. FORSYTH* AND R. L. DOWDELL,* MEMBER A.I.M.E.

(New York Meeting, February 1940)

A SEARCH through the available literature shows that the cobalt-nickel-silicon system has not been systematically studied. This seems rather odd because all three elements are fairly abundant and have better than average corrosion resistance; however, they have high melting points, which makes experimental work difficult. Cobalt and nickel form a continuous series of solid solutions and each metal dissolves about 7.5 per cent silicon.

Many ternary alloys have been studied and the results have been published in a great many different ways, but to present such data in a short but clear and understandable manner is still a problem. The following pages describe the results of the study of 76 alloys from which the partial ternary diagram (Fig. 1) of the cobalt-nickel-silicon system has been drawn.

The alloys were chosen according to the plan in Fig. 1a by taking definite ratios of cobalt and nickel, such as 70 Ni, 30 Co or 40 Ni, 60 Co, and adding silicon in various percentages. Each section was studied in detail by means of thermal analysis and microscopic examination, but only two of these detailed sections were thought necessary in the point perspective drawing to give a comprehensive picture of the liquidus, solidus and solid transformations that take place over the temperature ranges studied. Complete thermal analyses and microscopic data are given in Table 1.

EXPERIMENTAL PROCEDURE

The alloys were prepared from metals of commercial purity, as follows: electrolytic nickel 99.60 + 0.35 Co; chemically purified silicon 99.79 per cent plus impurities of Fe 0.027, Al 0.008, Ca 0.014, C 0.004, N₂ 0.10; and cobalt 98.82 per cent plus impurities of Ni 0.42, Fe 0.12, CaO 0.27, S 0.012, Mn 0.10 and SiO₂ 0.15. It should be noted that the largest impurity in cobalt is nickel, one of the alloying elements.

The alloys were melted in a small Ajax induction furnace, the nickel and cobalt being melted first because of their better ferromagnetic

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properties and the silicon being slowly added to the melt. Addition of silicon too rapidly caused overheating and loss of silicon. Fine-

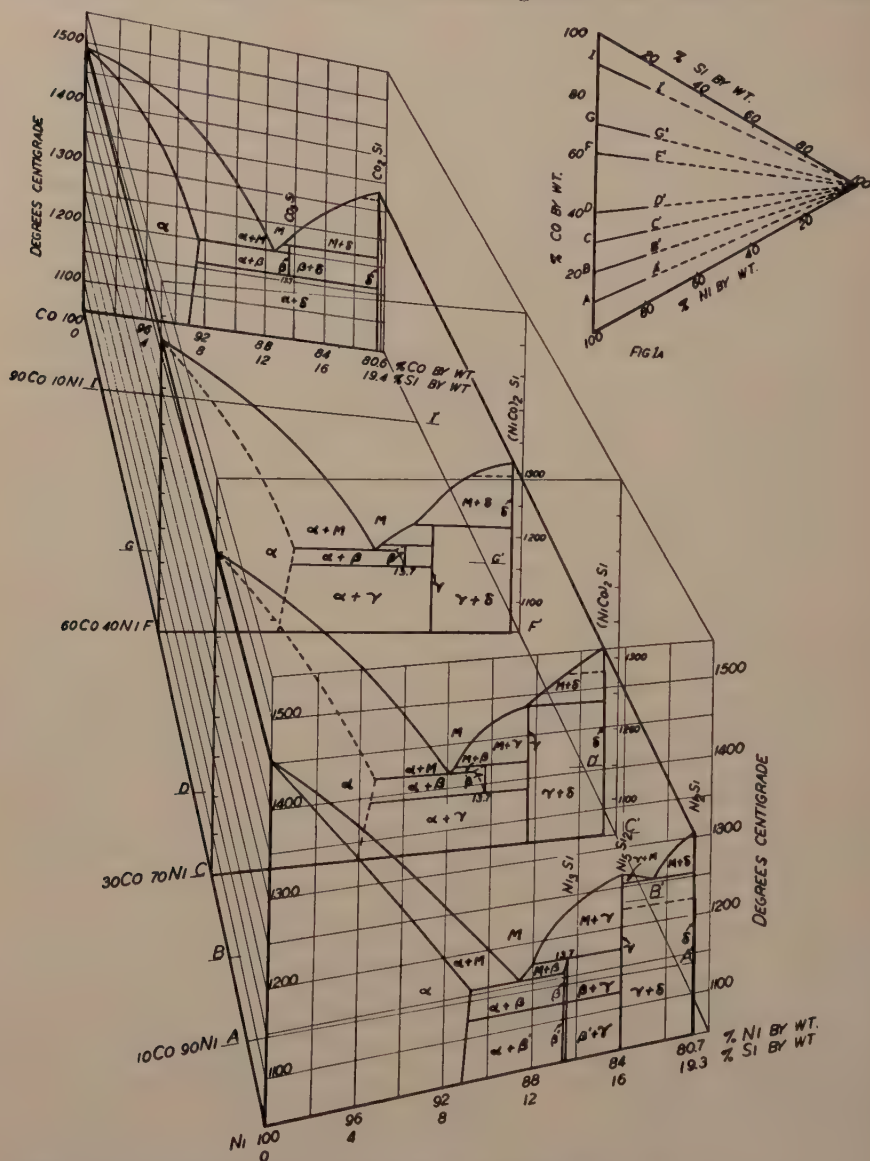


FIG. 1.—POINT PERSPECTIVE DRAWING OF COBALT-NICKEL-SILICON SYSTEM BETWEEN 0 AND 19.4 PER CENT SILICON, WITH (UPPER RIGHT CORNER) SECTIONS INVESTIGATED IN DETAIL.

grained alundum crucibles were used. Remelting for thermal analysis was done in a carbon resistor furnace with alundum tubes as liners. Slightly reducing atmospheres were automatically obtained at all

times. Barium chloride was used as a cover to prevent contamination of the melt. A platinum-platinum + 10 per cent rhodium thermocouple was used for all thermal analysis determinations. It was standardized by the National Bureau of Standards with a stated accuracy of $\pm 5^{\circ}\text{C}$.

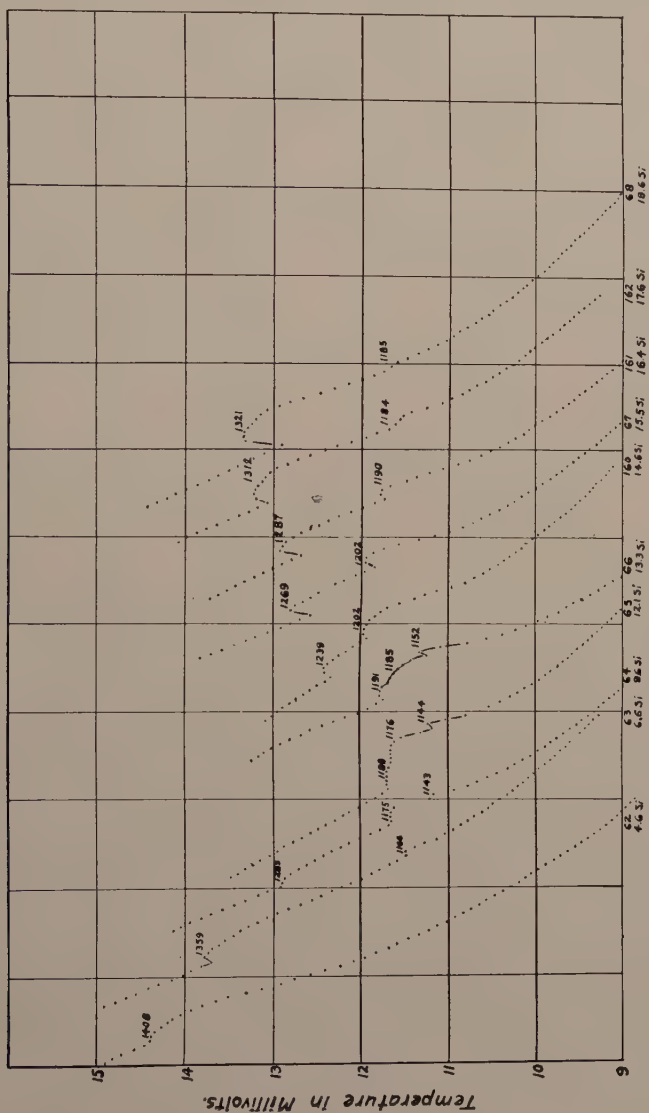


FIG. 2.—SOME TYPICAL TIME-TEMPERATURE COOLING CURVES FROM SECTION GG' , FIG. 1.

throughout its entire range. The couple was frequently checked for accuracy by N.B.S. pure copper (m.p. 1083°). Thermocouple readings were made with a potentiometer with accuracy of at least 0.01 mv. The average speed of cooling during thermal analysis was about 16°C .

per min. at 1250°C., decreasing to approximately 11°C. per min. at 1000°C. Supercooling was found with almost all alloys but could be overcome by stirring or slight vibration.

The data in Table 1 represent seven sections through the ternary diagram between zero and 20 per cent Si, as shown in Fig. 1a. Each section was plotted and studied in detail but all were found to be so much alike that two sections were thought sufficient to give the necessary connecting links between the two binary diagrams nickel-silicon and

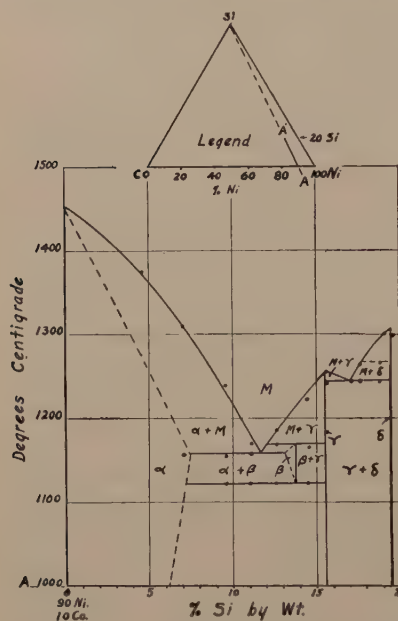


FIG. 3.

FIG. 3.—DETAIL OF VERTICAL SECTION AA', FIG. 1.

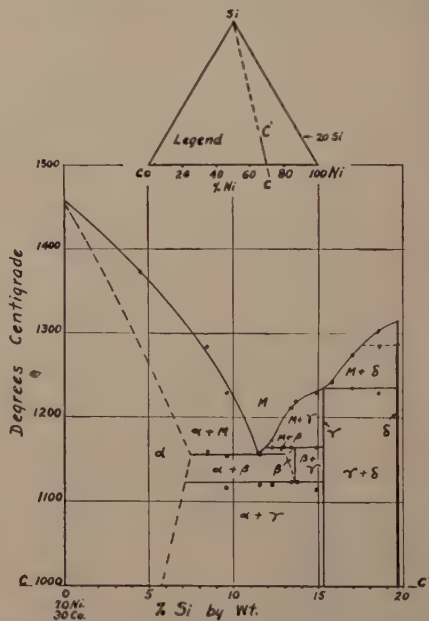


FIG. 4.

FIG. 4.—DETAIL OF VERTICAL SECTION CC', FIG. 1.

cobalt-silicon (Fig. 1). The changes from one section to the next were gradual and easily apparent.

However, since thermal cooling curves played such an important part in the development of this diagram, a few should be included. A representative series of time-temperature cooling curves is reproduced in Fig. 2 from alloys in section GG'. Only one curve is shown for each alloy but it was often necessary to make duplicate or triplicate curves where points were in question.

From the combined results of the cooling curves and the microscopic examination of each series of alloys, a vertical section was constructed. For illustration, four such vertical sections are reproduced in Figs. 3 to 6. These sections give a much more detailed picture of the transformations, the phases present, and the gradual changes in phase composition. The

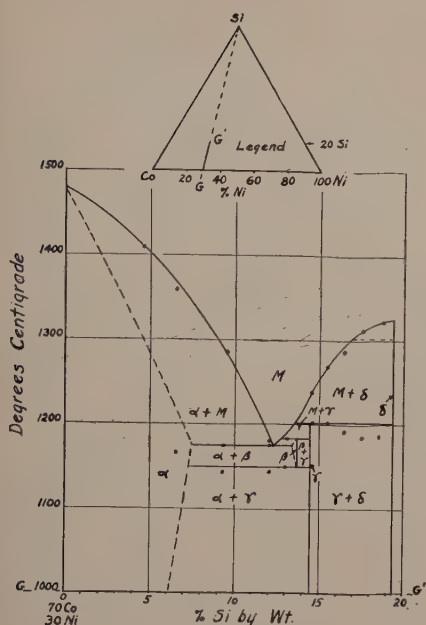


FIG. 5.

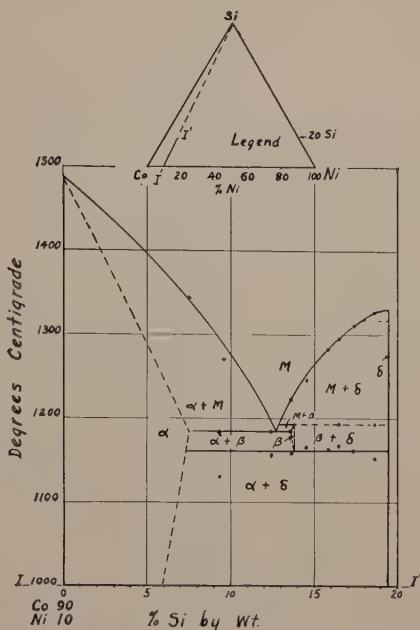
 FIG. 5.—DETAIL OF VERTICAL SECTION GG' , FIG. 1.


FIG. 6.

 FIG. 6.—DETAIL OF VERTICAL SECTION II' , FIG. 1.


FIG. 7.

FIG. 8.

 FIG. 7.—ALLOY 79.9 PER CENT NICKEL, 8.8 COBALT, 11.1 SILICON, CAST. $\times 500$.
 Showing slight amount of primary α (dark), the remainder $\alpha + \gamma$ eutectic.

 FIG. 8.—ALLOY 35.2 PER CENT NICKEL, 52.8 COBALT, 11.6 SILICON, CAST. $\times 500$.
 Showing eutectic of α (dark) $+ \gamma$ (light).

 Etchant: 10 grams FeCl_3 and 30 c.c. concentrated HCl in 120 c.c. water.

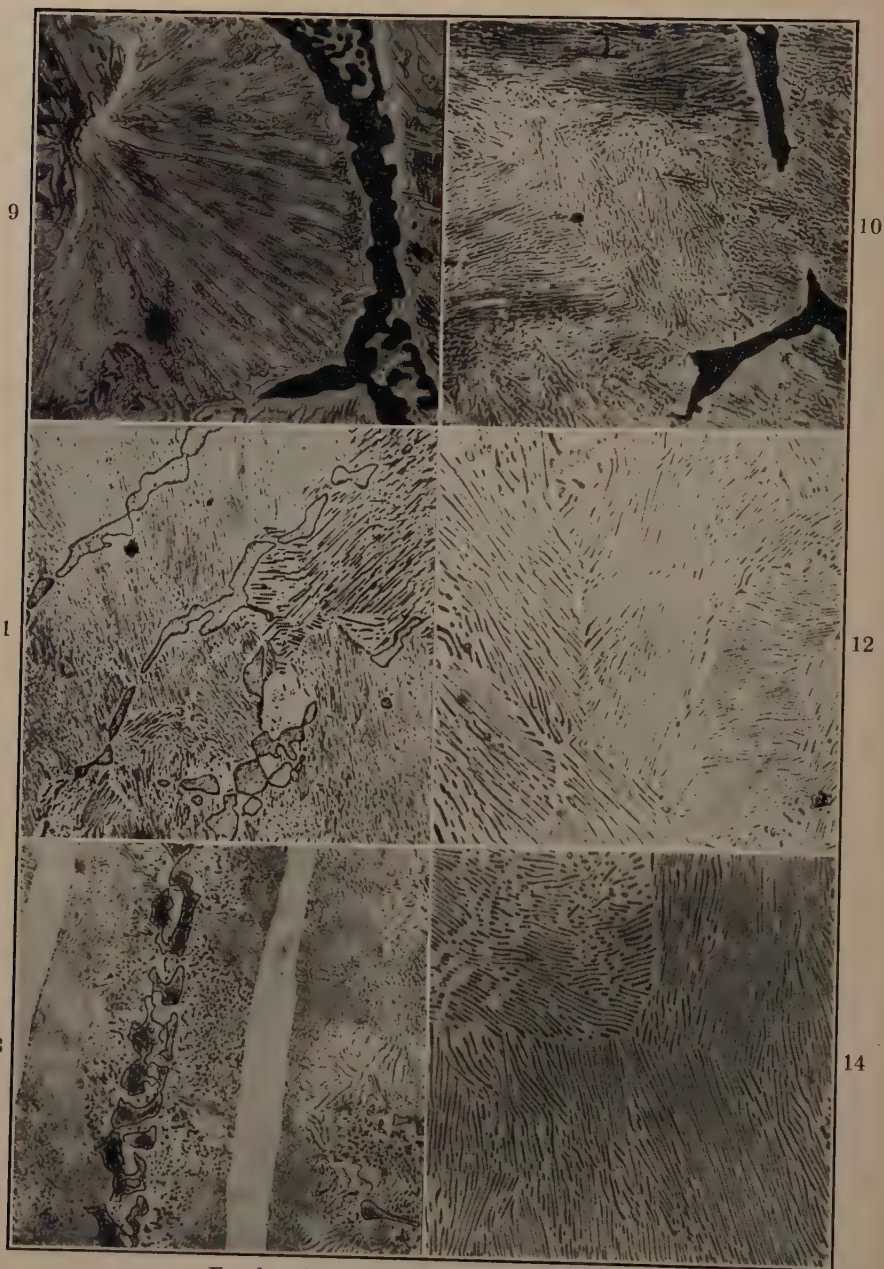
TABLE 1.—*Data of Thermal Analysis and Structure*

Alloy Designation	Nominal Composition, Per Cent			Transformations, Deg. C.				
	Ni	Co	Si	Primary	Eutectic	Eutectoid	Peritectic	Poly-morphic
A	Bal.		9.6	1199	1156	1121		
H	Bal.		12.1	1178	1156	1123		
Z	Bal.		13.5	1228		1125	1175	
B	Bal.		14.6	1248		1125	1170	
I	Bal.		16.0 ^a	1266		1120		
C	Bal.		17.1	1257	1154			
K	Bal.		17.4 ^a		1255			
J	Bal.		18.0	1274	1256			
L	Bal.		18.6	1289	1250			1226
D	Bal.		19.2 ^a	1306	1243			1228
SECTION AA'								
9	85.7	9.6	4.6	1375				
104	83.5	9.2	7.1	1310	1158			
10	81.3	8.9	9.6	1240	1156	1123		
105	79.9	8.8	11.1	1170	1159	1123		
12	78.5	8.7	12.6 ^a	1187	1156	1123	1168	
11	76.9	8.5	14.6	1222	1164	1121		
106	76.0	8.2	15.6	1258	1240			
13	74.5	8.1	17.1		1244			
107	74.1	8.0	17.6	1268	1244			
108	73.0	8.0	18.8	1301	1242			1266
14	72.0	7.9	19.7	1298				
SECTION BB'								
18	76.4	18.8	4.6	1366				
23	73.8	18.2	7.8	1275	1152			
19	72.3	18.0	9.6	1220	1155			
20	68.9	17.3	13.0 ^a	1205		1125	1165	
124	69.1	17.1	13.5	1211		1125	1164	
21	68.3	16.9	14.6	1240				
26	66.2	16.4	17.2	1272	1247			
22	64.3	16.0	19.5	1306				
SECTION CC'								
27	66.8	28.4	4.5	1373				
306	64.0	27.3	8.5 ^a	1284	1160			
28	63.3	26.8	9.6	1229	1154	1116		
33	61.9	26.3	11.6 ^a		1154	1118		
29	61.5	26.0	12.3 ^a	1172		1120	1164	
301	60.5	25.8	13.4	1213		1124	1163	
295	60.3	25.6	13.8	1220			1163	
30	59.6	25.3	14.9 ^a	1228		1114	1163	
34	58.4	25.2	15.7 ^a	1240				
31	58.1	24.6	17.1 ^a	1275			1234	
35	57.0	24.1	18.6 ^a	1304			1228	1284
32	56.0	24.0	19.7 ^a	1314				1288

TABLE 1.—(Continued)

Alloy Designation	Nominal Composition, Per Cent			Transformations, Deg. C.				
	Ni	Co	Si	Primary	Eutectic	Eutectoid	Peritectic	Poly-morphic
SECTION DD'								
39	56.3	37.2	6.2	1339	1270 ^b			
40	54.7	36.4	8.6	1282				
41	52.6	35.0	12.1 ^a	1165	1160			
42	52.2	34.8	12.7 ^a	1185	1160	1133	1168	
43	50.7	33.1	15.8	1236			1224	
44	50.4	31.9	17.2	1291			1226	
SECTION FF'								
50	38.1	57.0	4.6	1400				
51	36.6	54.5	8.6	1301	1172			
52	35.2	52.8	11.6	1184	1175	1150		
53	34.5	51.5	13.5	1208		1155	1182	
150	34.0	51.0	14.6	1227		1152	1208	
153	33.8	50.5	15.3 ^a	1254			1213	
54	33.6	50.2	15.9 ^a	1263			1221	
151	33.5	49.5	16.6	1296			1212	
152	32.9	49.1	17.6	1305			1210	
55	32.4	48.5	18.6	1287			1199	
SECTION GG'								
62	28.8	66.2	4.6	1408				
63	28.0	65.0	6.6	1359	1166			
64	27.2	62.8	9.6	1285	1175	1143		
65	26.5	61.0	12.1	1180	1176	1144		
66	26.0	60.4	13.3	1191		1152	1185	
160	25.6	59.5	14.6	1239			1202	
67	25.3	58.9	15.5	1269			1202	
161	25.1	58.2	16.4	1287			1190	
162	24.8	57.1	17.6	1312			1184	
68	24.4	56.5	18.6	1321			1185	
SECTION II'								
91	9.4	82.5	7.6	1347	1183	1123		
92	9.2	80.7	9.6	1271	1183	1130		
93	9.0	78.2	12.3		1183	1156		
94	8.8	77.1	13.6	1222	1182	1158		
191	8.6	76.3	14.6 ^a	1245		1167		
95	8.5	75.2	15.8 ^a	1282		1164		
192	8.4	74.5	16.5	1297		1169	1188	
190	8.3	74.0	17.3	1311		1160		
96	8.1	72.8	18.6	1327		1150	1188	

^a Determined by chemical analysis.^b Solidus.



For descriptive legends see opposite page.

most pronounced change occurs in gamma. As cobalt replaces nickel both the formation temperature and the silicon content of this phase decrease. From the information so far available the gamma phase becomes less stable at low temperatures when more than 61 per cent Co has been added. In section *II'* homogeneous gamma has not yet been preserved at room temperature and it has been assumed that gamma and beta decompose in the same manner and that gamma and beta intersect at the binary ratio of Co_3Si .

The binary diagrams of cobalt-nickel, cobalt-silicon and nickel-silicon have been reported in the literature and seem to be quite well worked out. The cobalt-nickel diagram, as reported by Ruer and Kaneko,¹ has been reproduced as part of Fig. 1. There is general agreement that the liquidus and solidus are separated by only two or three degrees centigrade and are represented by a single line.

The cobalt-silicon system, as reported by Vogel and Rosenthal,² has likewise been reproduced and seems to agree with ternary alloys with small percentages of nickel.

The latest work on the nickel-silicon diagram has been reported by Osawa and Okamoto³ and the section between 0–19.3 per cent Si is reproduced here, except that some of the transformation temperatures were found to be higher. For example, the δ phase, 19.3 per cent Si, froze at 1306°C . Temperatures of all transformations when different were plotted as found by the authors.

In Fig. 1 the phases represent continuous solid solutions or intermediate homogeneous phases. For example, α varies in composition from α containing only nickel and silicon to α containing only cobalt and silicon. Likewise, δ varies in composition² from 19.3 per cent Si + 80.7 per cent Ni to 19.35 per cent Si + 80.65 per cent Co. Furthermore, the designated phases in binary systems seldom agree and must be changed to correspond with those found to be continuous in the ternary.

FIG. 9.—NICKEL-SILICON BINARY ALLOY (13.5 PER CENT SILICON) HEATED TO 1135°C ., HELD 80 MINUTES, FURNACE-COOLED. $\times 200$.

FIG. 10.—ALLOY 13.5 PER CENT SILICON, 4.3 PER CENT COBALT, 82.0 PER CENT NICKEL. SAME TREATMENT AS FIG. 9. $\times 200$.

FIG. 11.—ALLOY 69.1 PER CENT NICKEL, 17.1 COBALT, 13.5 SILICON. SAME TREATMENT AS FIG. 9. $\times 200$.

FIG. 12.—ALLOY 34.5 PER CENT NICKEL, 51.5 COBALT, 13.5 SILICON, HEATED TO 1170° FOR $\frac{1}{2}$ HOUR AND FURNACE-COOLED. $\times 500$.

Structure is all eutectoid. Slight amount of α present but not shown.

FIG. 13.—ALLOY 26.0 PER CENT NICKEL, 60.4 COBALT, 13.3 SILICON. QUENCHED IN WATER FROM MELT. $\times 500$.

Structure primary γ surrounded first by $\alpha + \gamma$ eutectoid, then $\alpha + (\text{eutectoid } \alpha + \gamma)$ eutectic.

FIG. 14.—SAME COMPOSITION AS FIG. 13; REHEATED TO 1175°C ., HELD 40 MINUTES, FURNACE-COOLED. $\times 500$.

Structure all $\alpha + \gamma$ eutectoid. Slight amount of α present but not shown.

Etchant: 10 grams FeCl_3 and 30 c.c. concentrated HCl in 120 c.c. water.

¹ References are at the end of the paper.

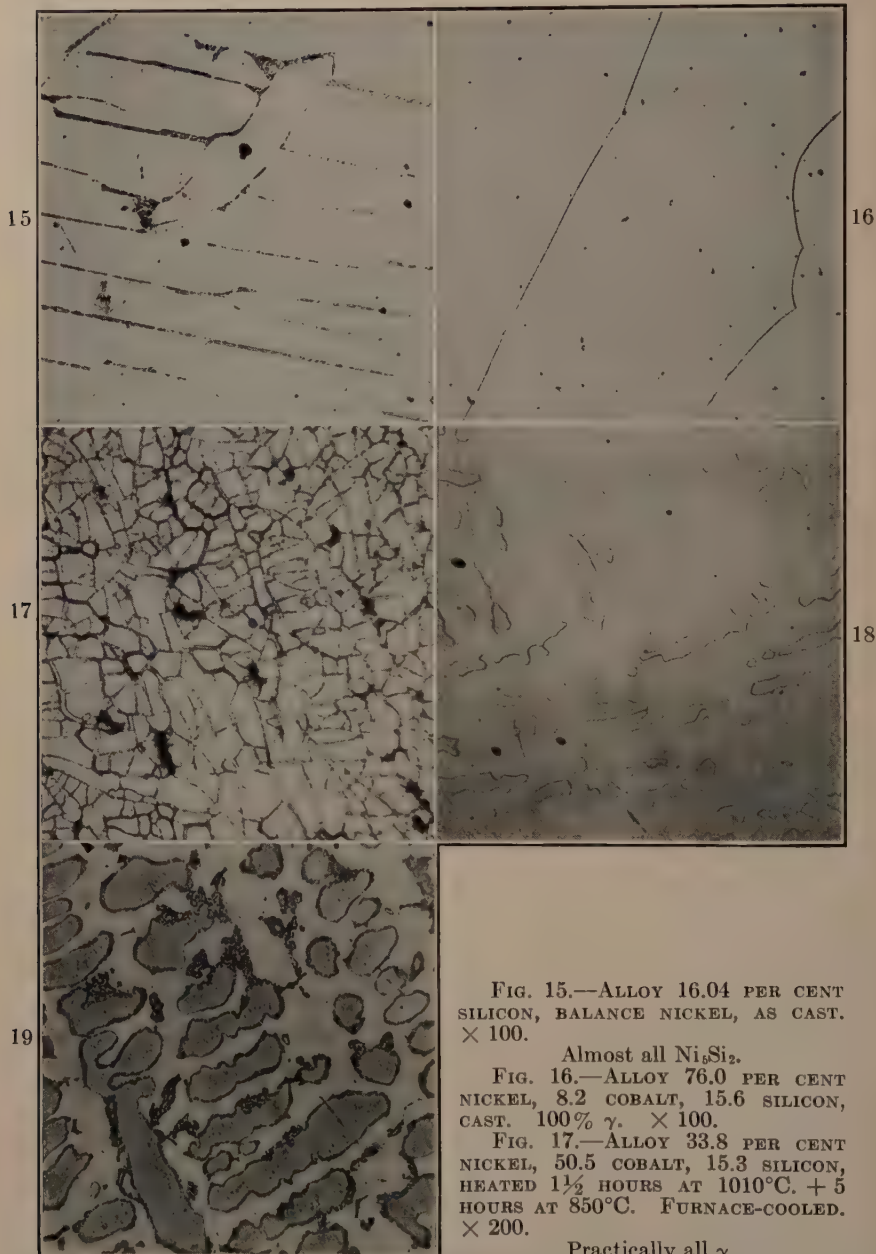


FIG. 15.—ALLOY 16.04 PER CENT SILICON, BALANCE NICKEL, AS CAST. $\times 100$.

Almost all Ni_3Si_2 .

FIG. 16.—ALLOY 76.0 PER CENT NICKEL, 8.2 COBALT, 15.6 SILICON, CAST. 100% γ . $\times 100$.

FIG. 17.—ALLOY 33.8 PER CENT NICKEL, 50.5 COBALT, 15.3 SILICON, HEATED $1\frac{1}{2}$ HOURS AT 1010°C . + 5 HOURS AT 850°C . FURNACE-COOLED. $\times 200$.

Practically all γ .

FIG. 18.—ALLOY 25.3 PER CENT NICKEL, 58.9 COBALT, 15.5 SILICON, HEATED 2 HOURS AT 1060°C . $\times 200$. FURNACE-COOLED.

Some primary δ , remainder γ .

FIG. 19.—ALLOY 25.1 PER CENT NICKEL, 58.2 COBALT, 16.4 SILICON. $\times 500$.

Consists of primary δ surrounded first by reaction rims and then γ .

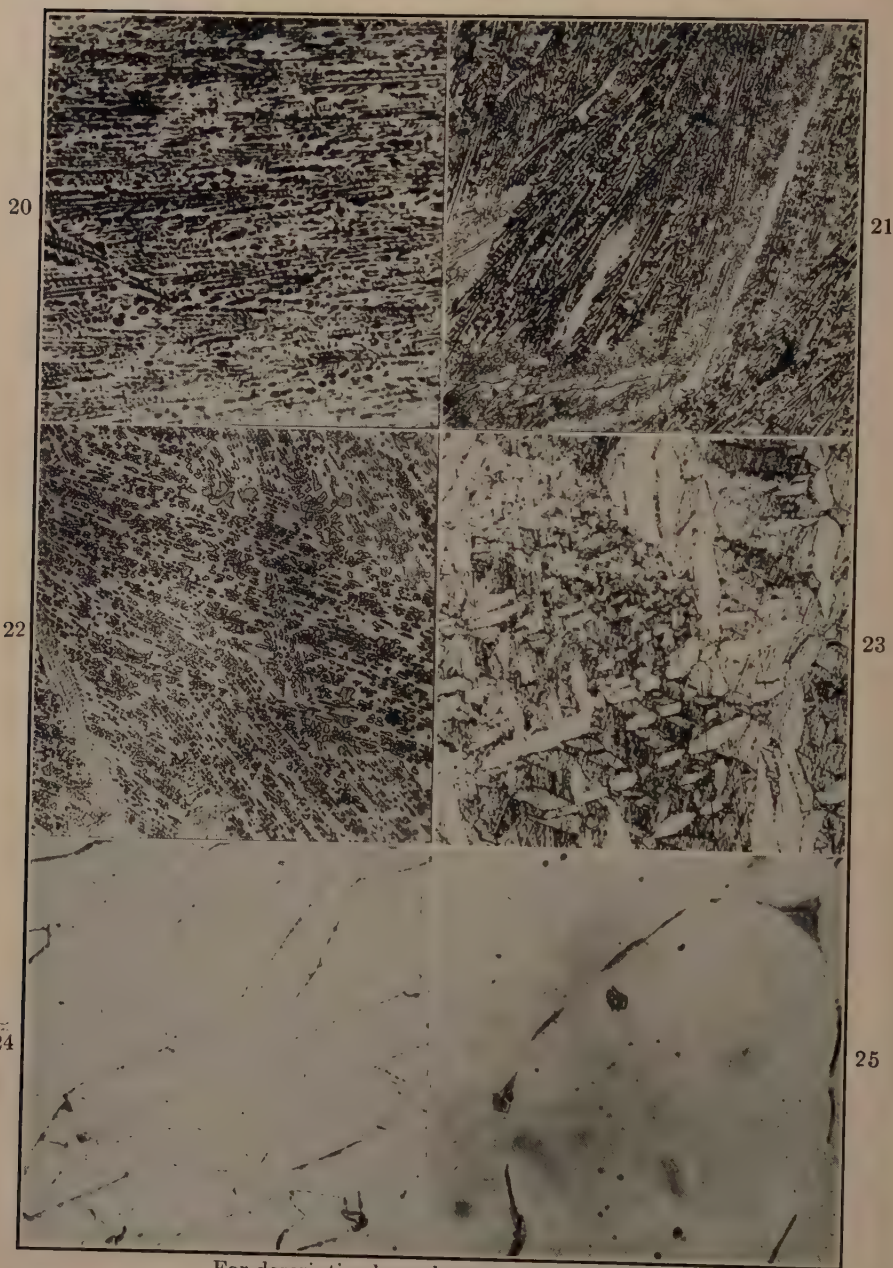
Etchant: 10 grams FeCl_3 and 30 c.c. concentrated HCl in 120 c.c. water.

The results of microscopic examination can be discussed best by beginning with the nickel-cobalt binary system and describing the changes brought about as silicon is added. The limits of solubility of silicon in different ratios of nickel and cobalt for maximum solubility at high temperatures and decrease of solubility, as temperature is lowered, have not been studied at great length. Further detailed work is now being done and will be available in the near future. Two alloys, one at 64.0 Ni, 27.3 Co, 8.5 Si and the other 9.5 Ni, 82.5 Co, 7.6 Si, show the solubility in a general way. After casting, both were reheated and held between 1130° and 1148°C. for 4 hr. and then water-quenched. Microscopic examination showed the latter to be a complete solid solution, designated as α , while the former contained about 10 per cent of β . Hardness determinations were made and the two alloys again reheated to 1040°C. and cooled slowly in the furnace. The result was an increase in hardness of about 15 per cent for the high-nickel alloy and 45 per cent for the high-cobalt alloy. No doubt changes in treatment will alter these results. Microscopic examination after the slow cooling treatment showed a fine spheroidized precipitate resolved by a high-powered objective.

The low-silicon eutectic in the ternary system, beginning at the binary nickel-silicon eutectic containing 11.5 per cent Si, gradually and uniformly increases in silicon content until the cobalt-silicon binary eutectic is reached, where the silicon content is reported to be 12.5 per cent. The melting point also rises gradually from the nickel-silicon eutectic at 1156°C. to the cobalt-silicon eutectic at 1200°C. The base of the eutectic valley between the two binary eutectics is nearly a straight line and no ternary eutectic alloy was found. Apparently nickel and cobalt are interchangeable and, consequently, only two phases appear in this eutectic structure. Figs. 7 and 8 illustrate the microstructures of two alloys in the ternary valley.

The phase relations in all the alloys studied are rather simple. In the as-cast condition three phases often appear but one can be eliminated by homogenizing below the solidus.

The next general microstructure of interest comes at a composition corresponding to the ratio Ni_3Si , $(\text{NiCo})_3\text{Si}$, or Co_3Si . The reaction that occurs here (no X-ray determinations made) is that of a eutectoid. In the nickel-silicon binary system, however, Osawa and Okamoto³ found that the structure was homogeneous (AuCu_3 type) instead of eutectoid. As cobalt replaces nickel, the silicon remaining almost the same, the structure appears more and more like a eutectoid reaction that is stable at low temperatures, since all structures were produced by slow cooling. Reheating for 2 hr. seems only to coarsen the structure. The microstructures in Figs. 9 to 14 inclusive show definitely that, at least when cobalt is present, the result is a eutectoid ($\beta = \alpha + \gamma$).



For descriptive legends see opposite page.

Vogel and Rosenthal² found that in the cobalt-silicon system the ratio Co_3Si , a compound, decomposed as a eutectoid. The illustration given by those authors was not decidedly lamellar but was definitely two phases. It seems reasonable, therefore, from the evidence available, to conclude that a eutectoid reaction takes place in the ternary system on a vertical plane between the two binary systems. The eutectoid temperature rises as cobalt replaces nickel. The eutectoid structures seem most easily obtained in alloys close to 60.4 Co, 26 Ni and 13.3 Si (Figs. 13 and 14). The alloy shown in Fig. 13 was melted and poured into water, where it chilled rapidly. The structure represents areas of primary γ surrounded by eutectoid $\alpha + \gamma$ and then by eutectic $\alpha + (\alpha + \gamma)$. This same alloy after reheating to 1175°C . for 40 min. transforms nearly completely to eutectoid (Fig. 14) when slowly cooled.

At 16 per cent Ni an intermediate phase occurs in the nickel-silicon system which corresponds to the compound Ni_5Si_2 . In the ternary system a continuous homogeneous alloy exists between Ni_5Si_2 and Co_3Si . It is stable at low temperatures as well as at high temperatures between Ni_5Si_2 and the alloy 25.3 Ni, 58.9 Co, 15.5 Si (Fig. 18), from which it probably becomes less stable at low temperatures, breaking up according to the eutectoid reaction, and coincides with the binary alloy Co_3Si . (The low-temperature transformations are not yet fully understood.)

Figs. 15 to 17 show the intermediate phase at various compositions on the ternary diagram. This intermediate phase (γ) on the nickel-silicon side is an open maximum. As cobalt replaces nickel and the composition of the alloy changes toward Co_3Si , the melting point gradually decreases. Simultaneously with this decrease of temperature, and at a composition of about 58.4 Ni, 25.2 Co, 15.7 Si (CC' , Fig. 1) this intermediate phase changes its mode of formation from open maximum to peritectic. It is illustrated in section FF' , Fig. 1. The photomicrograph in Fig. 19 shows reaction rims corresponding to the reaction.

The eutectic between γ and δ in the nickel-silicon system contains 17.4 per cent Si by weight and checks previous work closely. When

FIG. 20.—ALLOY 17.4 PER CENT SILICON BY WEIGHT, BALANCE NICKEL. $\times 100$.
Eutectic structure.

FIG. 21.—ALLOY 74.5 PER CENT NICKEL, 7.8 COBALT, 17.1 SILICON, CAST. $\times 100$.
Almost all eutectic $\gamma + \delta$. Freezing point, 1244°C .

FIG. 22.—ALLOY 67.2 PER CENT NICKEL, 16.8 COBALT, 16.5 SILICON. CAST. $\times 100$.
Structure almost all eutectic but eutectic disappears rapidly with increased cobalt additions.

FIG. 23.—BINARY ALLOY, 19.2 PER CENT SILICON, BALANCE NICKEL. CAST. $\times 100$.
Peculiar structure probably due to polymorphic change.

FIG. 24.—ALLOY 72.0 PER CENT NICKEL, 8.0 COBALT, 19.7 SILICON. ANNEALED.
 $\times 500$.

Structure solid solution δ .

FIG. 25.—ALLOY 24.3 PER CENT NICKEL, 56.7 COBALT, 18.6 SILICON. CAST AND ANNEALED. $\times 200$.

Small amount of γ at grain boundaries, remainder δ .

Etchant: 10 grams FeCl_3 and 30 c.c. concentrated HCl in 120 c.c. water.

nickel is gradually replaced by cobalt, forming three component alloys, the composition of the eutectic approaches that of γ and disappears when about 25 per cent Co by weight has been added. Figs. 20, 21 and 22 show the eutectics for three different alloys along the eutectic valley. The solidification temperature of the eutectic decreases as cobalt is added in a similar manner to that of γ but not as rapidly.

A single phase exists between the compounds Ni_2Si and Co_2Si according to the evidence obtained from thermal analysis and microscopic examination. The thermal analysis curves show that these alloys freeze at constant or nearly constant temperatures; Co_2Si freezes at 1332°C . while Ni_2Si was found to freeze 26°C . lower, at 1306°C ., and the freezing points of alloys between fall very closely on a straight line drawn between the two. The structure of Co_2Si has been reported as rhombic (*rhombisches*, Hansen) and that of Ni_2Si as orthorhombic (Osawa and Okamoto) which also indicates homogeneity.

This series of alloys goes through a transformation thought to be polymorphic in nature, at a temperature slightly below its freezing point, and varies from 12° to 78°C ., depending on the composition. Figs. 23, 24 and 25 show three different alloys in the series. In Fig. 25 the alloy is not entirely homogeneous because the percentage of silicon is below the required amount.

CONCLUSIONS

1. A partial cobalt-nickel-silicon constitution diagram below 19.3 per cent Si has been presented.

2. The method used in drawing this diagram shows clearly the liquidus, solidus and solid transformations for the temperature ranges investigated.

3. Nickel and cobalt seem to replace each other in these alloys, producing only two phases in stable equilibrium.

The following general observations were made during the investigation:

4. The α solid solution alloys are all capable of being wrought and may find industrial application. Their properties are now being investigated.

5. Alloys above 10 per cent Si are brittle but have excellent corrosion resistance and have properties that are being exploited.

6. Alloys containing α are ferromagnetic.

ACKNOWLEDGEMENT

The authors wish to acknowledge their indebtedness to Dr. H. S. Jerabek, Dr. J. C. Sanderson and Miss C. H. Green, all of the Institute of Technology, University of Minnesota, for helpful suggestions and splendid cooperation; to the International Nickel Co. and the Electro

Metallurgical Sales Corporation for pure metals, and to Mr. W. E. Apuli, of the Mines Experiment Station, for chemical determinations.

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DISCUSSION

(Eric R. Jette presiding)

F. N. RHINES,* Pittsburgh, Pa.—In a case like that studied by Forsyth and Dowdell, the phase rule may provide a general check upon the validity of the experimental observations and may indicate the probable existence of reactions that otherwise would escape observation in a complicated alloy system.

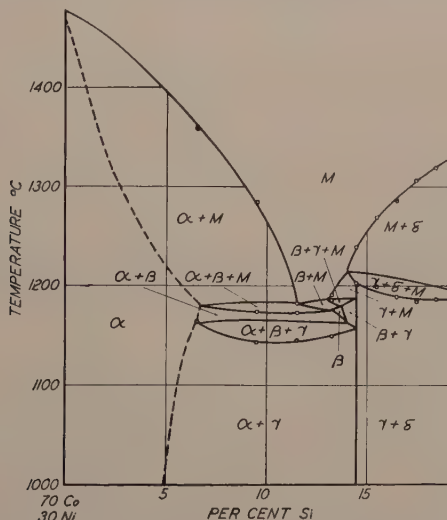


FIG. 26.—REDRAWING OF FIG. 5, SHOWING HOW THREE-PHASE REGIONS MAY BE SUBSTITUTED FOR ISOTHERMAL REACTION LINES IN THE SECTION, AND AT THE SAME TIME CAUSE LINES TO PASS THROUGH A MAJORITY OF THE DATA POINTS.

According to the phase rule, the sections of Figs. 3, 4, 5 and 6 of this paper should be expected to contain no truly horizontal straight lines except by the merest chance, whereby it would appear preferable to draw all lines as curves through the data points, unless there is reason to suspect the validity of some of the points. The horizontal straight lines of Figs. 3, 4, 5 and 6 should also be replaced by three-phase fields bounded by three curved lines. There is another rule of construction, leading to the same conclusion, which states that two-phase regions may meet in the ternary space diagram only along lines and not along surfaces, whereby it follows that all two-phase regions should be separated by one-phase or three-phase regions except at *points* of contact (or along lines in the binary or quasibinary sections). Fig. 5 of the paper has been redrawn (Fig. 26) to illustrate the application of these rules.

* Metals Research Laboratory, Carnegie Institute of Technology.

In view of the degree of supercooling indicated in the sample cooling curves of Fig. 2, it is not surprising that evidence of the existence of the small three-phase regions was not found. Microscopic evidence of the three-phase reactions is to be sought in a system of this type only in the occurrence of coring in the duplex cast structures, such as those of Figs. 7, 8 and 19. Since metallographic tests for coring are frequently unreliable, the best hope of showing this effect probably lies in a search for the widening of diffraction lines that would result from the existence of a concentration range in each phase of the structure.

I should like also to offer a plea for the use of isothermal sections in the presentation of ternary alloy data. There are several advantages of the horizontal over the vertical section that we in America seem to be slow to appreciate and utilize. The isothermal section is simpler in its geometry, because three-phase regions appear as straight-sided triangles, and, as a result, it is possible to interpolate between data points with more confidence. More important to the user of the diagram, the phases that may be present under any given set of conditions are all shown in the isotherm, while they are not shown in the vertical section. For example, in an alloy containing 10 per

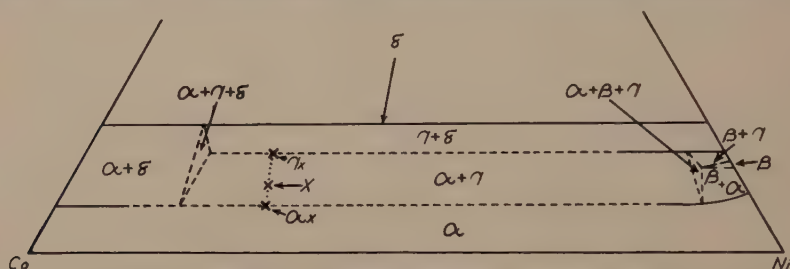


FIG. 27.—ISOTHERMAL SECTION AT 1100°C., SHOWING GENERAL FORM OF DIAGRAM ON COBALT-NICKEL SIDE

Tie line $\tau_x - \alpha_x$, passing through alloy composition x , does not, in all probability, lie in the direction of any of the sections drawn in the paper, even though one such section may pass through the composition x .

cent Si + 27 per cent Ni + 63 per cent Co at 1100°C., Fig. 5, the phases are seen to be α and γ , but the α is, in all probability, not any α shown in Fig. 5 but one containing either more or less of each of its three components than is represented in this section; likewise, the composition of the γ probably does not occur in this section. In the isotherm at 1000°C. (Fig. 27), on the other hand, all compositions of all phases that may occur at this temperature are shown, and the compositions of the α and γ occurring in the alloy in question are indicated by the ends of the tie line passing through the gross composition point. Thus the actual solubility limits may be read from the isothermal section, whereas they may not be read from the vertical section.

A. C. FORSYTH AND R. L. DOWDELL (authors' reply).—We are grateful to Dr. Rhines for calling attention to the possibility of α , β and γ coexisting in equilibrium as shown in Fig. 26. We had the phase principles in mind but were unable to establish any sections with three phases in equilibrium. The thermal analysis curves likewise indicate that the reactions in the region of possible three-phase equilibria take place within very narrow temperature limits. The research, however, is not a closed book and additional thermal analysis and heat-treatment are contemplated. This system cobalt-nickel-silicon, is of considerable interest and we hope Dr. Rhines and others will do further work.

Extrusion of Tin and Its Alloys

BY GERHARD DERGE,* JUNIOR MEMBER A.I.M.E., AND J. WARREN STEWART†

(New York Meeting, February 1939)

EXTRUSION processes are used in the commercial production of a wide variety of products, as indicated by the review presented a few years ago by D. K. Crampton.¹ Most writers have confined themselves to a general description of the equipment and products and the engineering aspects of the process. The few studies that have dealt with the metallurgical side of extrusion have been concerned primarily with an examination of the mode of flow of the metal during extrusion. This has been accomplished by the use of composite billets, by scribing grids on symmetrical sections of billets and observing the change of dimensions in the gridwork, or by examining microstructures in extruded sections.²⁻⁸ Another limitation of these original studies is that they were confined to the extrusion of very simple shapes, usually rods having a diameter of about one-fourth that of the billet.

Tin is particularly well suited to the extrusion of collapsible tubes and similar shapes in which the extruded section is very small in comparison to the diameter of the billet or slug. In modern production, impact extrusion methods are generally employed, therefore the thickness of the slug is small compared to its diameter. Under these conditions the process differs considerably from the processes that have been most fully described in the literature, and it is known that the quality of the product is very sensitive to slight variations in any one of the many variable factors involved, such as composition and structure of the alloy, rate of extrusion, temperature, shape of punch and die.

An exhaustive examination of all of the above-mentioned problems promises to produce so many data that it seems advisable to initiate the reports at this time, even though all of the factors outlined have not been examined fully, and to confine this paper to a description of the apparatus and method. Only tin and its alloys with small amounts of copper have been considered. These are the alloys most commonly used in this country for the production of the type of articles already described.

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¹ References are at the end of the paper.

EXPERIMENTAL METHOD

The operation of the entire apparatus is illustrated in Fig. 1. The extrusion press proper, *B*, is set into a hydraulic testing machine *A-A'*. The punch or ram of the press operates a set of two levers *C*, so that its movement is magnified 50 times before transmission by a steel tape to the autographic recorder *D* of the tensile machine. In this way, a stress-strain curve is obtained for the complete extrusion cycle. The punch may be made to move at chosen constant rates, or a constant

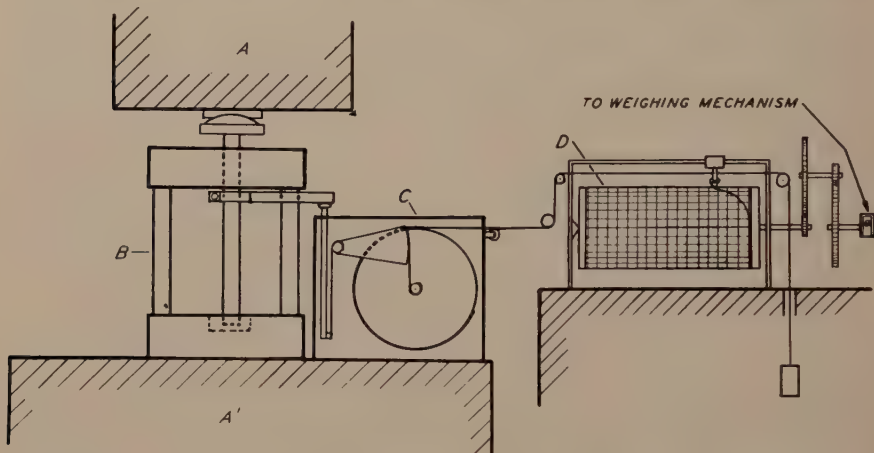


FIG. 1.—APPARATUS USED FOR MEASURING FORCES AND RATES OF EXTRUSION.

A, A', hydraulic testing machine.

B, extrusion press.

C, extensometer.

D, drum for recording autographic curve.

extruding force may be applied. In either case the rate of movement is checked by a stop watch. In the work to be described, only a single set of tools was used, designed to give a tube with 0.995-in. outside diameter and 0.010-in. wall thickness. The compression faces of the die and punch were both flat. The slugs to be extruded were stamped from a sheet of the material required. They had a diameter of 0.980 in., were 0.140 in. thick, and extruded into a tube about 3 in. long.

With the exception of some high-purity material, which will be described separately, all of the tin was cut from the same ingot of Chempur tin.* To obtain tin slugs, this was remelted and kept at 500° C. under charcoal for 3 hr. before casting into cylindrical iron molds. These rods were reduced 15 per cent by rolling and annealed for 2 hr. at 200° C. to destroy the cast structure before rolling down to the slug thickness.

* A typical analysis of this material is given in the Statistical Yearbook, 1938, page 6, International Tin Research and Development Council. The estimated purity is 99.9919 per cent.

The copper alloys were all prepared by adding the required amount of a 20 per cent copper alloy of which the composition had been established by analysis. This high-copper alloy was prepared by the addition of O.F.H.C.* copper to Chempur tin. The alloys were cast, rolled and punched in a manner comparable with that used on the tin, and the 200° C. anneal was prolonged to 48 hr. to secure better homogenization. To ensure uniform lubrication conditions, the slugs were all washed with acetone and then covered with vaseline. Just before extrusion the vaseline was removed as thoroughly as possible with a clean cloth.

A few slugs were made from some high-purity tin prepared by the fractional distillation of C. P. stannic chloride. The apparatus was constructed entirely from Pyrex glass and consisted of: (1) a one-liter boiling flask attached by a ground joint to (2) a 5-ft. fractionating column, 1 in. in diameter, packed with "Penn State rings" (small glass spirals $\frac{1}{4}$ in. in diameter wound from $\frac{1}{16}$ -in. solid rod); (3) a Friedrichs reflux condenser; (4) a capillary tube acting as a control valve, the diameter adjusted so that about eight-tenths of the condensed material was refluxed; (5) a one-liter collecting flask, which was protected from the moisture of the atmosphere by a calcium chloride drying tube. Three distillations were made at atmospheric pressure, and the first and last thirds of each were discarded. Two distillations followed with the pressure reduced to about 35 mm. of mercury; only the last thirds of these were discarded. Experience had shown that copper was eliminated rapidly by these vacuum distillations. The pure stannic chloride obtained in this way was added to distilled water and the tin deposited electrolytically on graphite electrodes. Two platinum anode spirals were enclosed in Pyrex cloth sacks, which acted as risers on an air lift. This air lift was operated by tank hydrogen and served not only to circulate the electrolyte but also to discharge into the atmosphere the chlorine formed at the anodes. The deposit was stripped and melted under vacuum to a sound, gas-free ingot. Spectrographic analysis, by methods described in a separate publication,¹¹ showed 0.00006 per cent copper and detectable traces of bismuth and platinum, certainly not more than a few hundred thousandths per cent of each. No other elements could be detected.

RESULTS

The original stress-strain curves obtained from a series of pure tin slugs extruded at different speeds are shown in Fig. 2. During the first steep section of the curve *AB*, the slug is settled into the die, and the elastic strain in the machine is taken up. The extrusion of the tube occurs during the essentially flat part of the diagram, *BCD*. When the

* Oxygen-free high-conductivity.

curve begins to rise at *D*, the part of the slug left in the die has become thinner than the walls of the tube, and the metal must flow through an increasingly small orifice between the bottom of the die and the ram. The general shape of the curve seems to be typical of the process and to represent qualitatively the behavior of any particular tin alloy.

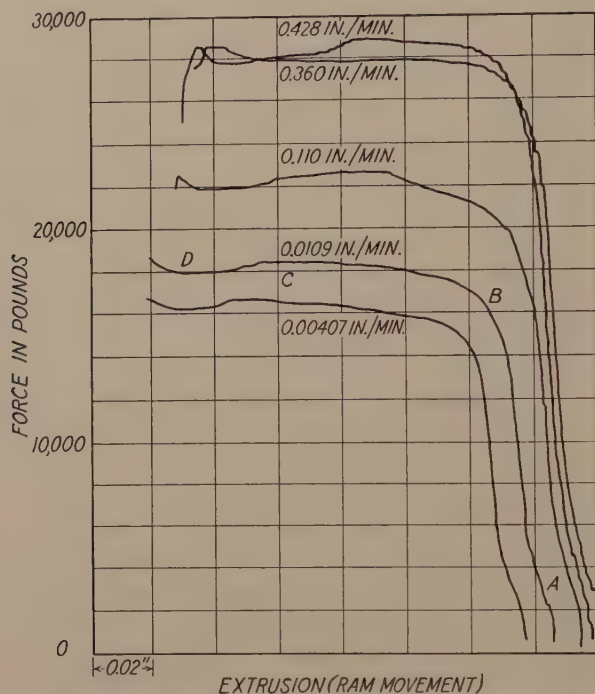


FIG. 2.—ORIGINAL AUTOGRAPHIC EXTENSION CURVES FOR CHEMPUR TIN AT VARIOUS EXTRUSION SPEEDS.

It was pointed out by Pearson and Smythe⁴ that if the logarithm of the extrusion pressure is plotted against the logarithm of the rate of extrusion, a straight-line relation is obtained for extrusion performed at any given temperature. This relationship has been found to apply very well to the data we have collected, and it seems to offer a most promising method for correlating the information at hand. Fig. 3 contains not only the curves for tin that have already been described, but also those for the high-purity tin, a series of copper alloys of hypoeutectic and hypereutectic and eutectic compositions, and a commercial 1 per cent copper alloy prepared from Straits tin. The extent to which the points on any particular curve deviate from the best straight line that can be drawn through them constitutes the best illustration of the accuracy of the method.

DISCUSSION OF RESULTS

Some features of the general shape of the extrusion curves illustrated in Fig. 2 should be given further consideration. The drop in pressure between the points *C* and *D* increases as the rate of extrusion increases, though occasional exceptions occur. The exact meaning of this drop does not seem to be certain. Pearson and Smythe⁴ extruded lead at constant pressures and observed similar effects—i.e., near the end of the billet the rate increased. Their equipment included thermocouples for

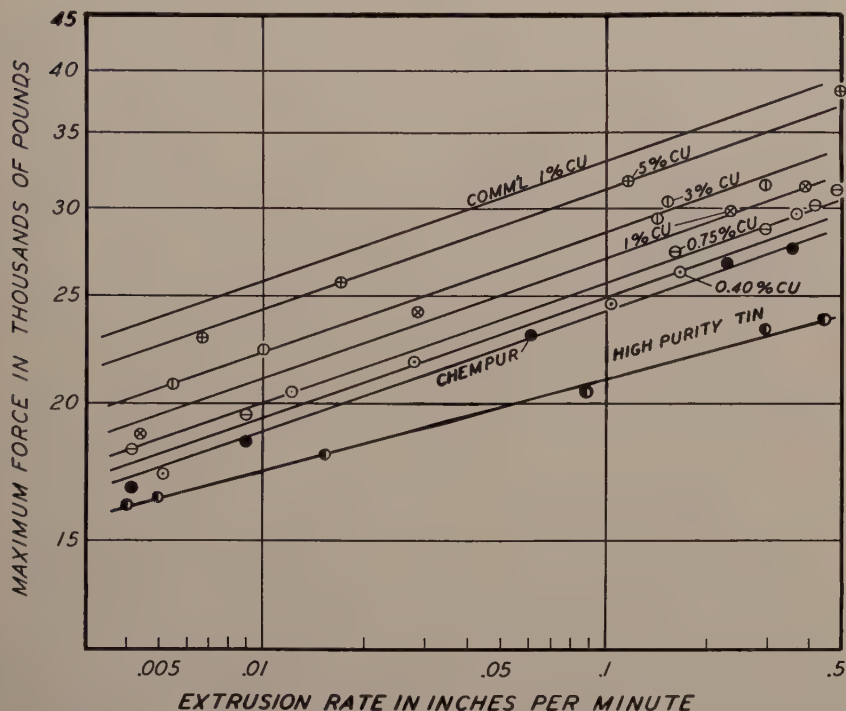


FIG. 3.—EXTRUSION RATE PLOTTED AGAINST MAXIMUM FORCE REACHED AT THIS RATE (LOG-LOG SCALE).

following the temperature of the billet and the extrusion block, and they did not observe any significant fluctuations. However, heating of the metal during extrusion and the development of preferred orientations during deformation must still be considered as possible explanations of this drop. Professor Siebel⁸ has published several curves, determined by the indirect extrusion of lead, which show a similar fall in pressure near the end of the extrusion. He attributes this to a fundamental change in the nature of the deformation process; namely, "from this point onward only the inner parts of the billet still flow in the delivered bar." Such an explanation does not seem satisfactory in the present

instance, for there is no reason to suppose that deformation ceases in the region furthest removed from the orifice when this diminution in pressure begins. Attention should be drawn to one feature of these curves obtained from lead, which is not found in the extrusion of tin. Just as lead extrusion begins, the pressure shows an appreciable drop to a steady value, which is maintained until near the end of the process. Dr. Crampton¹ cited data to indicate that free-cutting copper alloys also require an initial pressure higher than that during the bulk of the extrusion. There was no evidence of this initial drop in any of the work reported in this paper. Significant differences between the general behaviors of lead and tin during extrusion would not be expected, and this effect may not be important. At any rate, there do not seem to be any important work-hardening effects during the extrusion of tin, for once extrusion has begun the metal continues to flow with very little further increase in pressure.

The effect of alloying the tin with copper can be determined from a consideration of Fig. 3. The most recent value for the solid solubility of copper in tin at the eutectic temperature is 0.0063 per cent.⁹ An equally reliable value for room temperature does not exist, but the copper content of the tin used is about 0.001 per cent, and it is probable that this material can be said to represent the behavior of the solid solution of copper in tin. The alloy containing 0.40 per cent copper is then a typical hypoeutectic alloy. The eutectic composition, reported between 0.70 and 0.75 per cent copper,¹⁰ is represented by the curve for 0.75 per cent copper. The 1, 3, and 5 per cent copper alloys are definitely hyper-eutectic, the 1 per cent sample comparing with the composition range most generally used in production. Photomicrographs of these alloys are shown in Figs. 4 to 9 and indicate the range of structures examined. It is interesting to note that the curves for all of the copper alloys and for Chempur tin are parallel; i.e., the increase of pressure with extrusion rate is the same for these materials. However, the curve for the high-purity tin has less slope. Pearson and Smythe's plots⁴ show different slopes for different metals. One may therefore conclude that copper in solid solution alters this property of tin appreciably, but that the slope is not affected by the amount or distribution of the copper-tin phase. However, it is evident that the pressure required for extrusion at any given rate increases with the amount of copper added, and that beyond the eutectic this increase is roughly linear. For purposes of comparison, the curve for slugs taken from commercial production, containing about 1 per cent copper, is included in Fig. 3. Its slope is the same as that of the other alloys, but this material requires a considerably higher pressure at any given extrusion rate than the purer alloy of equal copper content. This difference may be assigned to the additional impurities normally present in commercial tin, as well as to those resulting from the additions

of small amounts of scrap. The differences between the curve for Chempur tin and the high-purity samples offer additional evidence of the appreciable effects of very small amounts of impurities upon the extrusion properties of a metal.

CONCLUSIONS

Consideration of these experiments leads at once to the conclusion that any influence leading to an increase in the slope of the pressure-rate curves described is to be avoided in practice where rates are normally



FIG. 4.—CHEMPUR TIN ETCHED IN 1 PART NITRIC ACID, 1 PART ACETIC ACID, 8 PARTS GLYCEROL. $\times 680$.

FIG. 5.—ALLOY OF TIN WITH 0.40 PER CENT COPPER, ETCHED IN ALCOHOLIC ACID FERRIC CHLORIDE. $\times 250$.

relatively high. However, the outstanding question is, how far can these pressure-rate curves be extrapolated legitimately? Obviously the method is not well suited to faster rates, and some independent studies will have to be made to determine the answer. It is known that in the range of speeds used in production the process is sensitive to the rate at which the metal is forced through the orifice and that a distinct advantage is gained by keeping the rates as low as the economics of the situation will permit. Therefore it seems probable that relations similar to those found in the present experiments still hold at the higher rates, and that the information derived from the slower experiments, where conditions

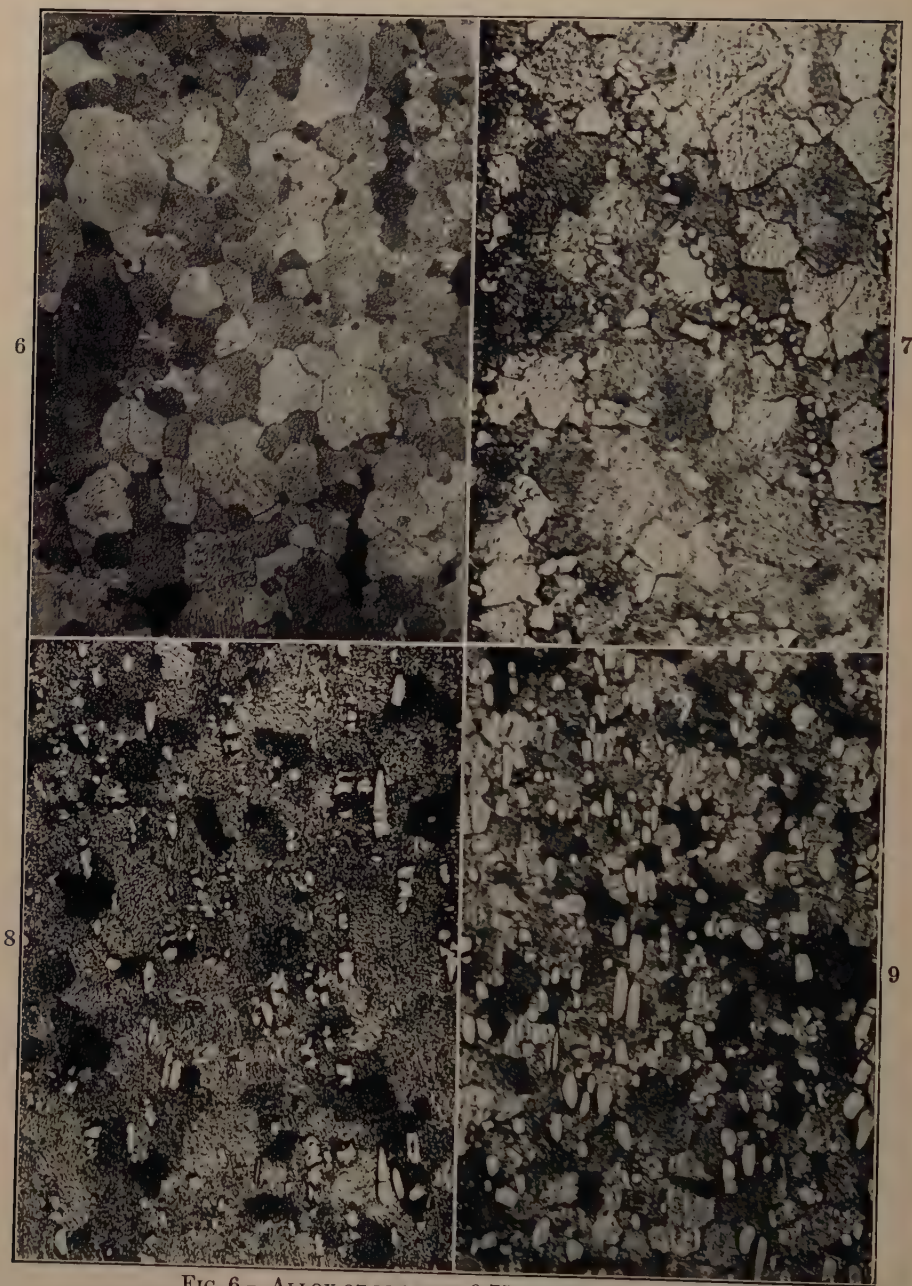


FIG. 6.—ALLOY OF TIN WITH 0.75 PER CENT COPPER.
FIG. 7.—ALLOY OF TIN WITH 1.0 PER CENT COPPER.
FIG. 8.—ALLOY OF TIN WITH 3 PER CENT COPPER.
FIG. 9.—ALLOY OF TIN WITH 5 PER CENT COPPER.
All etched in alcoholic acid ferric chloride. $\times 250$.

can be controlled more accurately, will be of value to the producers of extruded soft metal products.

SUMMARY

1. Equipment and methods are described for recording stress-strain curves during the slow extrusion of tubular products.
2. Data are recorded for tin and its alloys with copper in the range from 0 to 5 per cent.
3. These data produce straight lines when the logarithm of the rate of extrusion is plotted against the logarithm of the pressure.
4. The curves for the materials studied indicate that the slope is determined by the elements in solid solution in the tin.
5. The pressure required for extrusion at any given rate increases with the amount of copper present.
6. The limitations of the method and its other possible applications are discussed.

ACKNOWLEDGMENTS

The Bristol-Myers Company, of New York City, has sponsored the research program of which this investigation is a part.

Mr. J. H. Friden, of the Sun Tube Corporation, Hillside, New Jersey, constructed the special extruding equipment and has given much helpful advice.

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DISCUSSION

(Bruce W. Gonser presiding)

B. W. GONSER,* Columbus, Ohio.—The authors have made an excellent start in their study of factors influencing extrusion of tin and have produced some very interesting results. One factor, which appears to be of prime importance, is the composition of the tin used. Fig. 3 indicates that the commercial tin with but 1 per cent of copper requires a markedly higher force to effect extrusion than Chempur tin plus 5 per cent copper. This indicates that copper is by no means the chief constituent to influence extrusion rate. Commercial tin has not over 0.25 per cent and probably only 0.1 to 0.2 per cent of total impurities compared to approximately 0.01 per cent for Chempur. Evidently the tenth per cent or so total of antimony, arsenic, iron, lead, bismuth, or whatever may be present in the commercial tin, or their combination, in connection with the percentage of copper is more potent in resisting extrusion than adding 4 per cent more copper. It would be interesting to start with Chempur tin containing 1 per cent copper and add single impurities and combinations of impurities, to find which have the greatest effect on raising the force necessary for extrusion.

The fact that the authors have made tin of such purity that the known impurities total less than one part per million of tin is particularly worthy of recording.

D. K. CRAMPTON,† Waterbury, Conn.—This paper is particularly interesting because direct experimental evidence in connection with such procedures is scarce. It is recognized that this is the first of a series of such experimental studies and points brought up here will probably be considered in some work later on.

The difference between the shape of the curves in this paper and those for brass as reported by the present discussor in 1936 might possibly be explained in several ways. The data previously published on brass alloys were taken from commercial practice with the normal extrusion procedure where a rod (or tube) is extruded through a hole in the die ahead of the ram, whereas the present work is applied to the impact extrusion process, where there is no hole in the die but the metal flows back up around the ram as the latter is pressed into the slug in a solid-bottom die. Another point of difference is in the velocities in question. The present data were taken at ram velocities varying from 0.004 to 0.43 in. per minute, from which may be calculated roughly a tube velocity about 0.1 to 9.8 in. per min., or 0.008 to 0.8 ft. per min. The normal velocities through the die in commercial practice on brass vary from perhaps 20 ft. per min. as a minimum to as high as possibly 500 ft. per min. Even in the normal extrusion of pewter alloys through a die, velocities of 10 to 20 ft. per min. are used. The question is raised as to whether the shape of the curves shown by the authors would perhaps not be markedly altered at the very much higher velocities used commercially.

C. E. PEARSON,‡ Newcastle upon Tyne, England.—Although the behavior of metals when subjected to extrusion by hydraulic methods has been the subject of considerable scientific study, both as regards the nature of flow, the investigation of defects, and the influence of pressure and temperature on the deformation, very little progress has yet been made in examining the impact methods in the same way. The

* Metallurgist, Battelle Memorial Institute.

† Director of Research, Chase Brass and Copper Co.

‡ King's College, University of Durham.

fact that this is probably due to the greater experimental difficulties involved reflects to the credit of authors in starting the present investigation. It is gratifying to have independent confirmation of the exponential relationship of the rate of the extrusion to the extrusion pressure.

The question whether these results are capable of extrapolation to speeds such as are common in impact methods is complicated by the fact that a new factor becomes involved, that of temperature, which will upset the relationship. At low speeds of extrusion, such as have been used experimentally hitherto, this can be ignored, since any small amount of heat developed in the metal as the result of deformation is easily dissipated and the data therefore relate approximately to isothermal conditions. But this is not true under impact conditions, where the tubes coming from the press are decidedly hot; and this will naturally have a great effect on the resistance to deformation offered by the blank. I have found that, starting with cold billets of metals such as lead and tin and extruding by the inverted method at a fairly high speed, the pressure of extrusion, instead of remaining constant, falls rapidly during the stroke of the press and the issuing rod or tube is heated to 100°C. or higher. In the same way, one would expect that in an impact press the pressure on the punch would have a maximum value at the beginning of the stroke and would then diminish. It would be interesting if the authors could modify their autographic method to follow out pressure changes under impact conditions.

G. DERGE AND J. W. STEWART (author's reply).—Dr. Gonser has highlighted the importance of alloy composition very effectively and the experiments he has suggested are already near completion.

The differences between the experimental conditions in this paper and the conditions met in general commercial practice have been pictured clearly by Dr. Crampton. We are fully aware of these variations and intend to determine the importance of these factors.

The early work of Pearson and Smythe was very helpful to us and the fact that Professor Pearson has maintained an interest in extrusion problems throughout this period makes his discussion especially welcome. His suggestions are obviously in agreement with our ideas concerning the effects of speed and temperature on the extrusion pressure, as expressed in the discussion of results. His written discussion arrived somewhat late and we have already obtained measurements at high speeds which support these ideas. These data will be presented in detail soon, and it will suffice to say at this time that it has been found possible to measure extrusion pressures on a commercial impact press by using de Forest scratch extensometers. If a suitable correction is made for the temperature of the metal, the pressures obtained in this way fit the extrapolated curve as well as could be expected under the rather poorly controlled conditions, which did not allow an accurate determination of the temperature of the metal.

A Study of the Action of Molten Zinc Alloys on Pressure Die-casting Equipment

By E. A. ANDERSON* AND GERALD EDMUNDS,* MEMBERS A.I.M.E., AND C. W. SILLER*

(Chicago Meeting, October 1939)

IN the pressure die-casting of zinc alloys it is customary to force the molten alloy under high pressure into a permanent steel die by means of a plunger moving in a bushing that has a clearance on the diameter of the order of 0.002 in. Successful operation of the plunger type of machine requires the presence in the zinc alloy of certain percentages of aluminum. Without these aluminum additions, the normal reaction of molten zinc on ferrous materials causes sticking of the plunger and a complete shutdown of the equipment.

All of the zinc alloys used for pressure die-casting today contain approximately 4 per cent of aluminum, which is more than sufficient to make plunger operation feasible.

The clearance between the plunger and its bushing is an important matter. As the space becomes larger, there is a loss in effective metal pressure. Ordinary gray cast iron served fairly well and is still used in some machines. However, the rate at which the plunger clearance increases with this material is considered by many to be far too great. There is, therefore, a serious interest in finding new materials more capable of retaining the desired clearance during long periods of use. Today many die casters are using special materials for plungers and bushings selected by the somewhat expensive and time-consuming test of actual experience.

An analysis of the problem reveals two possible end points of plunger operation: (1) the building up of zinc-alloy plunger-material reaction products in sufficient bulk to cause sticking and (2) rapid solution, wear or erosion, all of which will increase the clearance to an undesirable extent. If neither of these takes place, the plunger will operate for a long time, of course.

The authors have developed a laboratory apparatus in which the action of a plunger moving in a bushing immersed in molten zinc alloy could be simulated closely. Such a machine made possible a more rapid and less expensive survey of the available construction materials and an analysis of the specific alloying reactions taking place in the clearance area.

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* Research Division, The New Jersey Zinc Co., Palmerton, Pa.

APPARATUS

The essentials of the apparatus are revealed in Fig. 1. Replaceable plunger *A*, 0.495 in. in diameter, is driven rapidly through replaceable

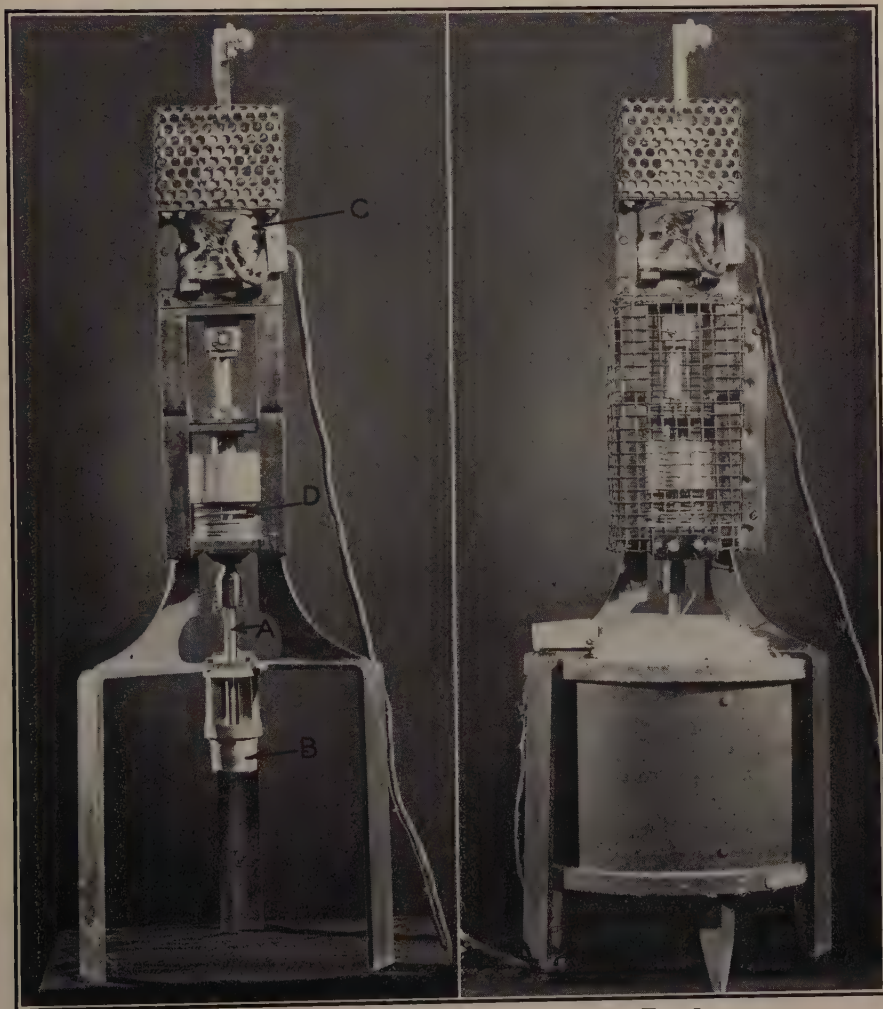


FIG. 1.

FIG. 2.

FIG. 1.—ESSENTIALS OF LABORATORY TEST APPARATUS.

FIG. 2.—GENERAL VIEW OF APPARATUS.

open-bottom bushing *B* by solenoid *C*. Spring *D* returns the plunger to the top of its stroke. The clearance on the diameter is 0.005 in. and the stroke is 1.5 in. The operation of the solenoid is controlled by a time switch, which functions every 30 sec., the plunger being held in the down

position for 3 sec. A counter records the number of strokes. The equipment as set up for operation is shown in Fig. 2.

In conducting a test the bushing and plunger are preheated and the top of the bushing, including the lower ends of the supporting arms, is submerged to a depth of $\frac{1}{2}$ in. in the molten zinc-alloy bath contained in a crucible in the furnace shown in Fig. 2. The assembly is held at a substantially constant temperature by means of an automatic controller connected to a thermocouple embedded in the walls of the furnace. The temperature of the bushing is measured by a chromel-alumel couple, the junction of which is placed in a drilled hole.

It is readily seen by those familiar with die casting that this apparatus closely simulates the operation of a die-casting machine, differing only in size and plunger clearance and in the fact that a die-casting plunger moves against pressure, whereas the laboratory test plunger does not.

A number of preliminary tests were carried out in which it was found that a strong tendency for a given plunger to stick in a particular zinc alloy was paralleled by outstanding difficulty in pressure die-casting the same alloy with plungers and bushings of the same test material. It is felt that within reasonable limits the test is thoroughly satisfactory as a means of predicting the sticking of plungers in practice and as a means of studying the alloying reactions occurring in the clearance area. Evaluation of the rate at which the clearance changes with use due to wear and erosion is not considered possible with any reasonable accuracy with the present equipment.

EXPERIMENTAL RESULTS

While the work is still in its preliminary stages, tests have been completed in duplicate using three different zinc or zinc-alloy baths and the following materials as bushings and plungers: (1) gray cast iron, from three different foundries; (2) nickel cast iron (1.2 per cent Ni); (3) cast stainless steel (18 Cr, 8 Ni, with less than 0.15 per cent C by specification); (4) wrought ingot iron; (5) nitrided Nitri-cast iron. All bushings and plungers in a given experiment were made of the same material and all test surfaces were machined. The zinc baths were, respectively: (1) pure unalloyed zinc held at 450° C., (2) zinc containing 0.25 per cent aluminum at 450° C., and (3) zinc containing 4.0 per cent Al at 420° C.

In each test the end point was the sticking of the plunger or the uninterrupted completion of about 11,500 cycles of operation (96 hr. of test). In some cases, after a test was completed the solidified zinc or zinc alloy was etched with hydrochloric acid from the plunger, to permit visual determination of the extent of attack on it. Portions of the parts were compared in the form of microspecimens in order to study the nature of the attack. The number of cycles of operation before sticking occurred in these tests are assembled in Table 1.

Table 1 reveals a number of interesting observations. For example, none of the ferrous metals tested except nitrided Nitri-cast iron made even limited operation possible in unalloyed pure zinc, whereas all except wrought ingot iron could be operated throughout the entire test period in the 4 per cent Al, 96 per cent Zn alloy. The cast stainless steel and nitrided Nitri-cast iron were outstandingly good in the tests in the 0.25 per cent Al alloy.

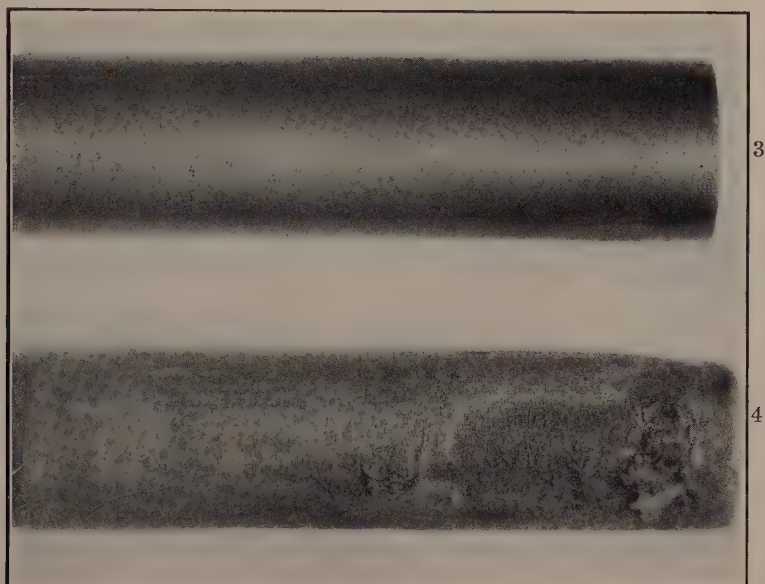


FIG. 3.—CAST IRON OPERATED 11,513 CYCLES IN 4 PER CENT ALUMINUM, 96 PER CENT ZINC ALLOY AT 420° C. $\times 2$.

FIG. 4.—WROUGHT INGOT IRON OPERATED 1717 CYCLES IN 4 PER CENT ALUMINUM, 96 PER CENT ZINC ALLOY AT 420° C. $\times 2$.

The difference in the attack of the 4 per cent Al alloy on cast iron and wrought ingot iron is clearly shown in Figs. 3 and 4.

MICROSTRUCTURES*

In most of the tests a microspecimen was prepared to contain the bushing, the plunger and the solidified zinc alloy in the clearance area between. Sometimes only the plunger or the bushing was sectioned.

Fig. 5 is typical of the structures observed in gray cast iron tested in unalloyed pure zinc. A solid mass of zinc-iron alloys has bridged the clearance gap and accounts for the sticking of the plunger early in

* Etched with 5 per cent Nital, except as follows: Fig. 8 was etched with 20 grams CrO_3 , 1.5 grams Na_2SO_4 , 100 c.c. H_2O ; Figs. 14 and 19 were etched with 5 grams CrO_3 , 0.4 gram Na_2SO_4 , 100 c.c. H_2O .

TABLE 1.—*Number of Cycles to Sticking of Plunger in Bushing in Experimental Trials of Apparatus*

Plunger-bushing Material	Test No.	Cycles to Sticking		
		Unalloyed Zinc	0.25 Per Cent Al Alloy	4.0 Per Cent Al Alloy
Cast iron No. 1.....	1	18	3,874	11,513 ^a
Cast iron No. 1.....	2	17	6,340	11,095 ^a
Cast iron No. 2.....	1	33	5,977	11,500 ^a
Cast iron No. 2.....	2	24	4,056	Not tested
Cast iron No. 3.....	1	25	5,774	11,510 ^a
Cast iron No. 3.....	2	36	4,943	Not tested
Average.....	..	26	5,161	^a
Nickel cast iron.....	1	27	3,216	11,516 ^a
Nickel cast iron.....	2	23	1,615	Not tested
Average.....	..	25	2,416	^a
Cast stainless steel.....	1	25	11,519 ^a	11,514 ^a
Cast stainless steel.....	2	23	11,259	Not tested
Average.....	..	24	>11,389	^a
Nitrided Nitri-cast iron.....	1	590	11,531 ^a	11,087 ^a
Nitrided Nitri-cast iron.....	2	552	Not tested	Not tested
Average.....	..	571	^a	^a
Wrought ingot iron.....	1	21	16	1,717
Wrought ingot iron.....	2	Not tested	15	873
Average.....	..	21	16	1,295

^a No sticking during test period.

the test. No evidence of selective attack along graphite streaks can be observed.

A similar structure resulted with nickel cast-iron parts, as is shown at higher magnification in Fig. 6.

The cast stainless steel likewise produced a complete conversion of the zinc to alloy (Fig. 7) but the appearance of the alloys differs somewhat from that observed in Figs. 5 and 6. The nitrided Nitri-cast iron resisted attack enough to permit operation for over 500 cycles, but, as is clear from Fig. 8, iron-zinc alloy finally formed in sufficient amount to cause sticking. The thin surface layer was not identified.

In the photomicrograph shown as Fig. 9, the wrought ingot-iron plunger only is shown with its adhering film of zinc-iron alloy.

With the addition of 0.25 per cent Al to the alloy definite changes developed in the appearance of the reaction products. Fig. 10 shows cast-iron parts after 5977 cycles in the 0.25 per cent Al alloy. Selective penetration along graphite streaks resulting in the separation of small

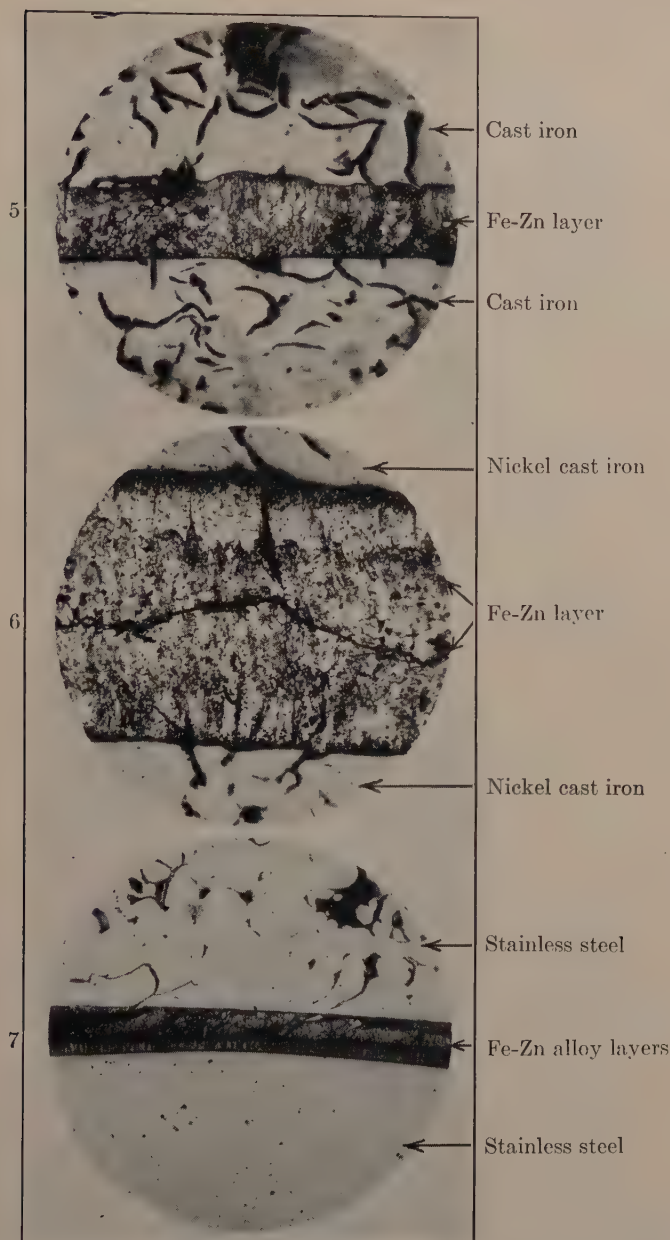


FIG. 5.—CAST-IRON PLUNGER-BUSHING AFTER 25 CYCLES IN UNALLOYED PURE ZINC AT 450° C. ORIGINAL $\times 200$.

FIG. 6.—NICKEL (1.2 PER CENT) CAST-IRON PLUNGER-BUSHING AFTER 27 CYCLES IN UNALLOYED PURE ZINC AT 450° C. ORIGINAL $\times 500$.

FIG. 7.—CAST STAINLESS-STEEL PLUNGER-BUSHING AFTER 23 CYCLES IN UNALLOYED PURE ZINC AT 450° C. ORIGINAL $\times 100$.

All reduced approximately $\frac{1}{5}$ in reproduction.

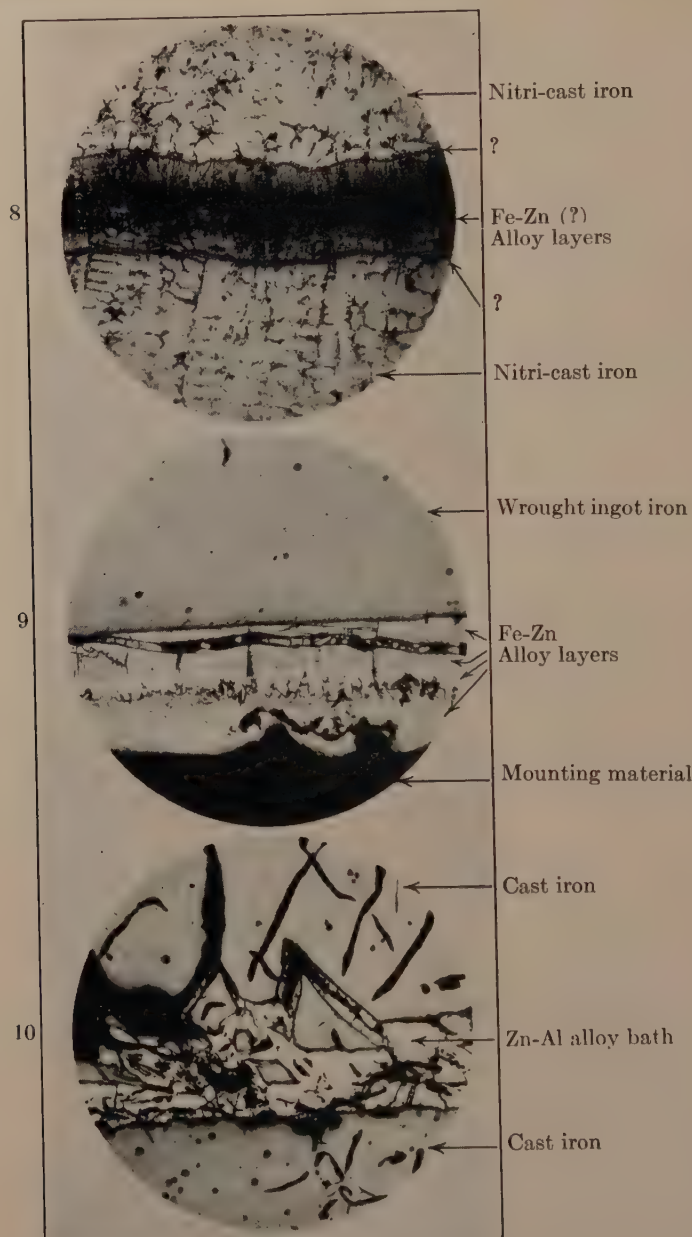


FIG. 8.—NITRIDED NITRI-CAST-IRON PLUNGER-BUSHING AFTER 552 CYCLES IN UNALLOYED PURE ZINC AT 450° C. ORIGINAL $\times 100$.

FIG. 9.—WROUGHT INGOT-IRON PLUNGER AFTER 21 CYCLES IN UNALLOYED PURE ZINC AT 450° C. ORIGINAL $\times 200$.

FIG. 10.—CAST-IRON PLUNGER-BUSHING AFTER 5977 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 200$.

All reduced approximately $\frac{1}{3}$ in reproduction.

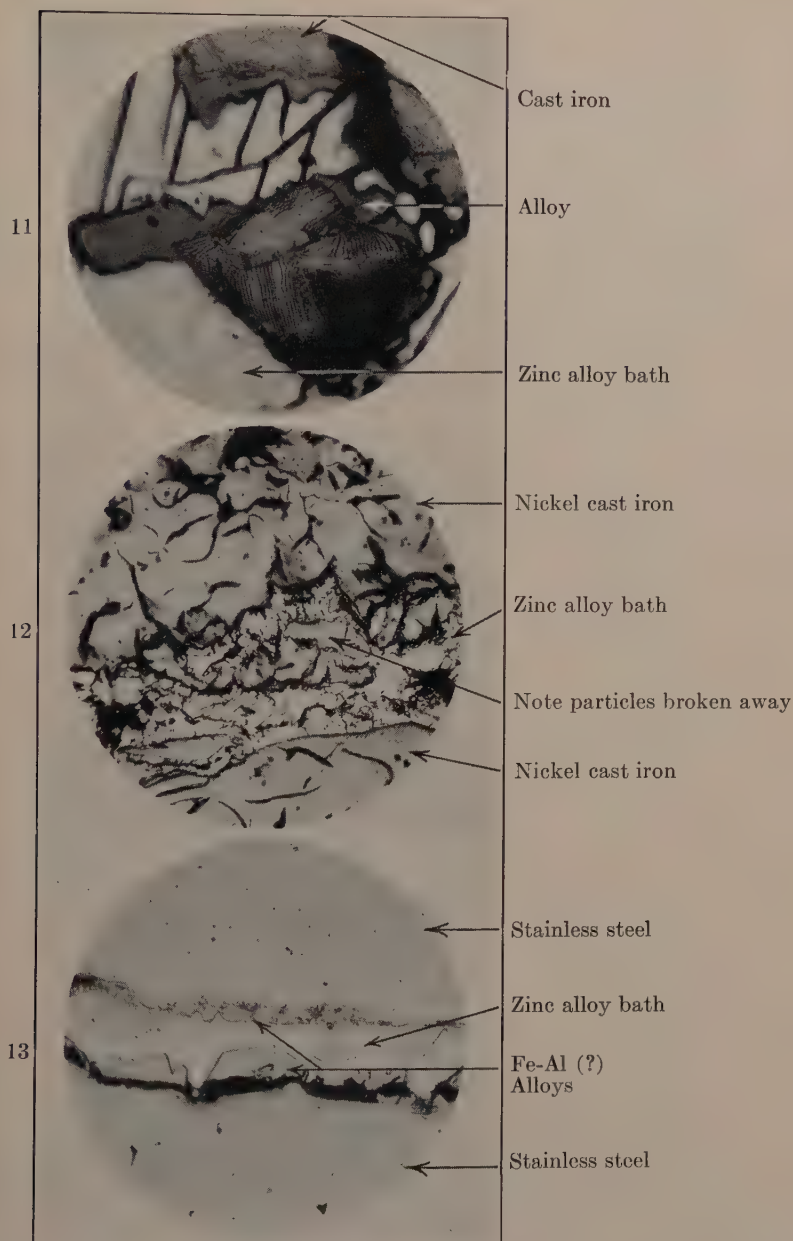


FIG. 11.—CAST-IRON PLUNGER-BUSHING AFTER 5977 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 1000$.

FIG. 12.—NICKEL CAST-IRON PLUNGER-BUSHING AFTER 1615 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 200$.

FIG. 13.—CAST STAINLESS-STEEL PLUNGER-BUSHING AFTER 11,259 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 100$.

All reduced approximately $\frac{1}{5}$ in reproduction.

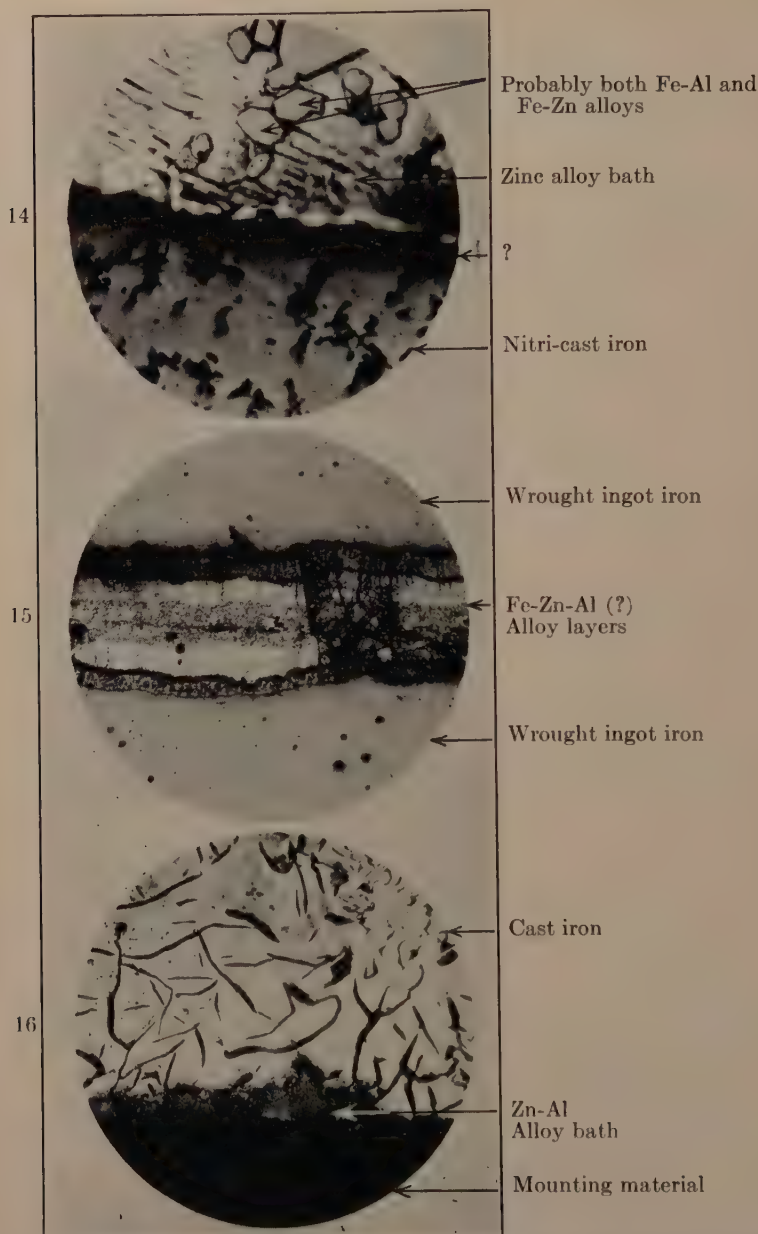


FIG. 14.—NITRI-CAST-IRON BUSHING AFTER 11,531 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 500$.

FIG. 15.—WROUGHT INGOT-IRON PLUNGER-BUSHING AFTER 16 CYCLES IN 0.25 PER CENT ALUMINUM ALLOY AT 450° C. ORIGINAL $\times 200$.

FIG. 16.—CAST-IRON PLUNGER AFTER 11,513 CYCLES IN 4 PER CENT ALUMINUM ALLOY AT 420° C. ORIGINAL $\times 100$.

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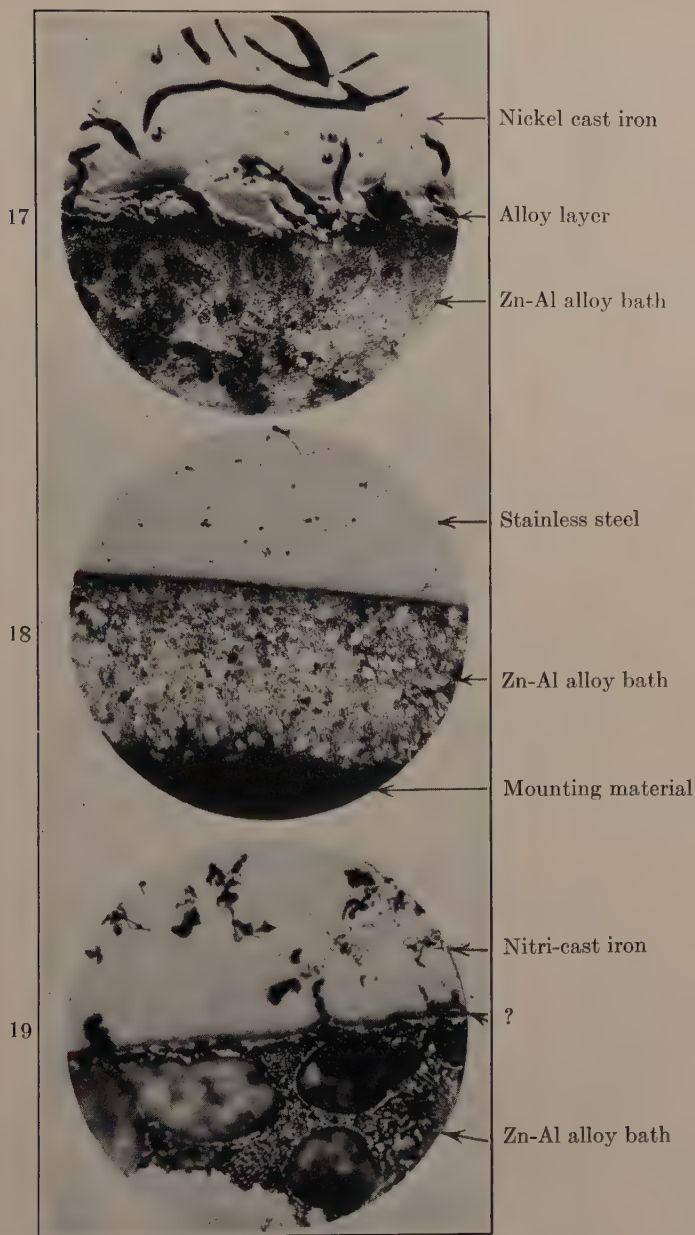


FIG. 17.—NICKEL CAST-IRON PLUNGER AFTER 11,516 CYCLES IN 4 PER CENT ALUMINUM ALLOY AT 420° C. ORIGINAL $\times 200$.

FIG. 18.—CAST STAINLESS-STEEL BUSHING AFTER 11,514 CYCLES IN 4 PER CENT ALUMINUM ALLOY AT 420° C. ORIGINAL $\times 100$.

FIG. 19.—NITRIDED NITRI-CAST-IRON BUSHING AFTER 11,087 CYCLES IN 4 PER CENT ALUMINUM ALLOY AT 420° C. ORIGINAL $\times 500$.

All reduced approximately $\frac{1}{5}$ in reproduction.

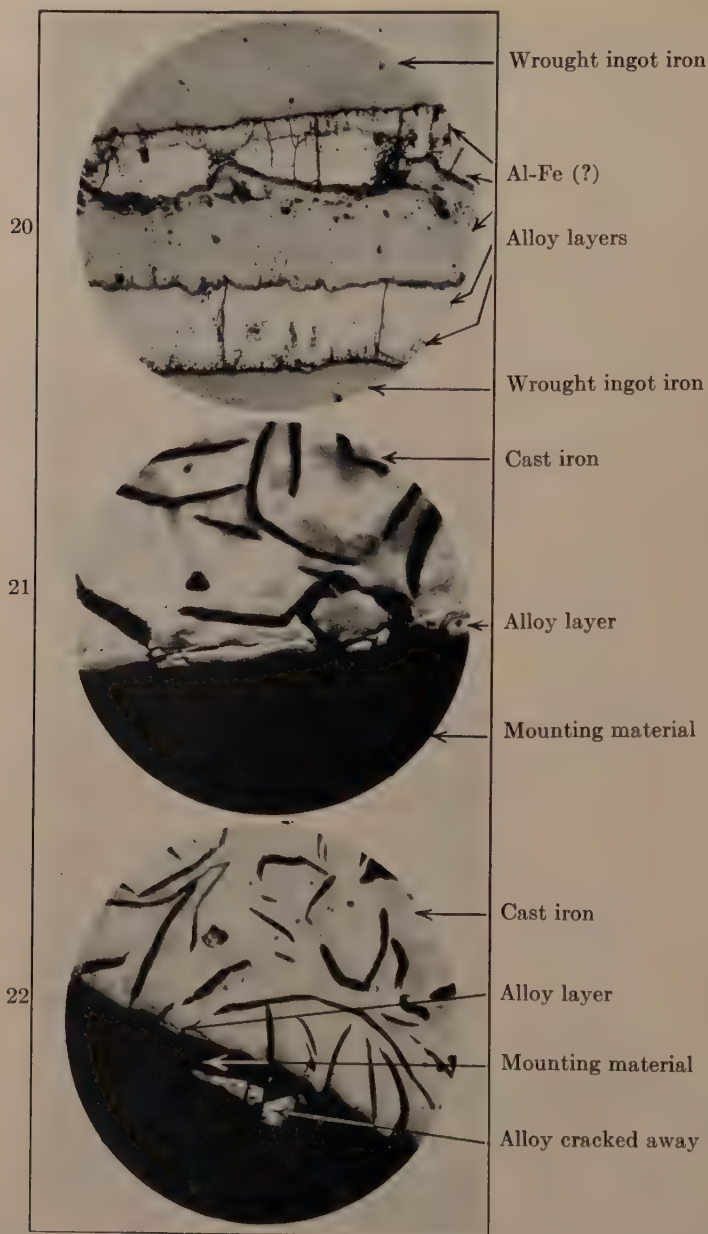


FIG. 20.—WROUGHT INGOT-IRON PLUNGER AND BUSHING AFTER 873 CYCLES IN 4 PER CENT ALUMINUM ALLOY AT 420° C. ORIGINAL $\times 200$.

FIG. 21.—SECTION FROM CAST-IRON (0.02 PER CENT NICKEL) BUSHING OF A COMMERCIAL DIE-CASTING MACHINE AFTER SERVICE IN ZINC ALLOYS CONTAINING 4 PER CENT OF ALUMINUM. ORIGINAL $\times 200$.

FIG. 22.—ANOTHER PART OF SAME BUSHING AS FIG. 21. ORIGINAL $\times 100$.

All reduced approximately $\frac{1}{2}$ in reproduction.

fragments of iron is evident. In Fig. 11, evidence is seen of the formation of a reaction product, presumably of iron and aluminum, since it shows none of the characteristics of known zinc-iron alloys.

The nickel cast iron reacted much as the gray cast iron did (Fig. 12). The stainless-steel parts were attacked with the formation of compounds as shown in Fig. 13. There appear to be two compound layers formed in the stainless-steel surface as well as large crystals of an additional compound extending into the melt.

The Nitri-cast iron, Fig. 14, shows no definite evidence of attack. Iron-zinc crystals present in the melt may have been formed by solution

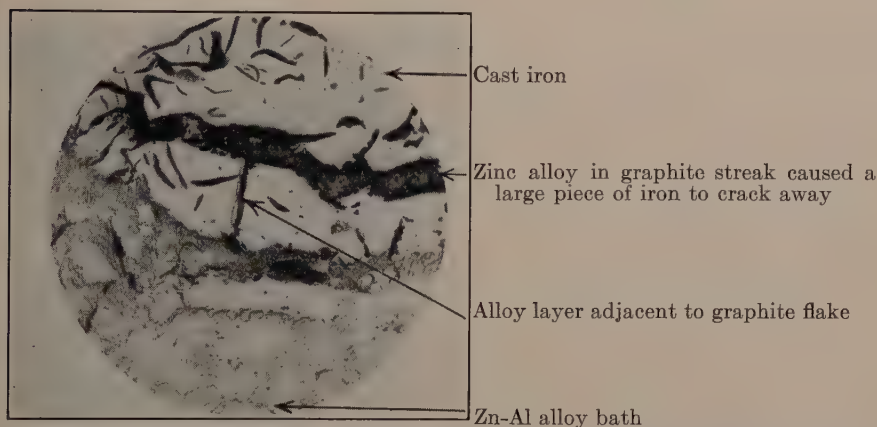


FIG. 23.—SECTION FROM CAST-IRON (0.46 PER CENT NICKEL) GOOSENECK OF COMMERCIAL DIE-CASTING MACHINE AFTER SERVICE IN ZINC ALLOYS CONTAINING 4 PER CENT OF ALUMINUM. ORIGINAL $\times 100$. REDUCED APPROXIMATELY $\frac{1}{2}$ IN REPRODUCTION.

of the cast-iron bushing holder rather than the plunger or bushing. The layer (dark) on the bushing surface may be the surface nitride.

In the wrought ingot iron, compounds more like the zinc-iron phases appeared (Fig. 15). It is possible that some form of ternary zinc-aluminum-iron compound is represented.

When the aluminum content of the zinc alloy was increased to 4 per cent, additional changes in the structure of the alloy in the clearance gap became evident. A typical cast-iron plunger section with adhering zinc-aluminum alloy is shown in Fig. 16. At 1000 diameters visual examination detected some indications of compound formation.

The presence of nickel (1.2 per cent) in cast iron resulted in more definite compound formation (Fig. 17). There is some evidence in this photomicrograph of the selective penetration along graphite streaks as shown in Fig. 12. The stainless steel, on the other hand, showed no indications of alloy formation even at 1000 diameters. A photomicrograph taken at 100X is shown as Fig. 18. As with the 0.25 per cent

Al alloy, Nitri-cast iron, Fig. 19, showed no apparent attack by the 4 per cent Al alloy.

The early sticking experienced with wrought ingot-iron parts operated in the 4 per cent Al alloy is readily understood from Fig. 20. The entire clearance gap is seen to be filled with compounds, probably of iron-aluminum, perhaps containing some zinc.

EXAMINATION OF PARTS OF COMMERCIAL DIE-CASTING MACHINES

During the course of this work, sections cut from pots, goosenecks, plungers and bushings that had been in service in die-casting machines operating with one or more of the standard zinc die-casting alloys containing 4 per cent of Al were studied. Of specific interest in connection with the subject matter of this paper are the microstructures found in two parts: (1) a cast-iron bushing of low nickel content (0.02 per cent) and (2) a cast-iron gooseneck containing 0.46 per cent of nickel. These parts had been in service in the same machine and therefore had received similar treatment.

The low-nickel cast-iron bushing reacted with the zinc alloy to produce a thin film of reaction product (probably compounded largely of iron and aluminum) which tended to crack away, leaving a new iron surface exposed to attack. Figs. 21 and 22 illustrate this effect. There was no indication of selective penetration along graphite streaks.

The reaction of the 0.46 per cent Ni cast iron with the zinc alloy was very similar to that noted in the laboratory tests with the 1.2 per cent Ni cast iron. A definite tendency is evident for alloying to take place along graphite streaks (Fig. 23) and for pieces of iron to separate in these areas and pass out into the melt.

The writers are unwilling at this time to draw the apparent conclusion that gray cast iron is superior to nickel cast iron for die-casting machine pots, goosenecks and plungers, because other factors not apparent here undoubtedly contribute heavily toward the final service life.

DISCUSSION

It would be premature at this time to attempt a precise evaluation of the reactions occurring in the clearance gap in the various tests, since no positive identification has been made of the compounds observed. It is clear from the tests, however, that the successful operation of a die-casting machine of the plunger type depends both upon the materials of which the plunger and bushing are constructed and upon the composition of the zinc alloy being die-cast.

The apparatus has fulfilled the purpose for which it was designed, but since it was not intended to evaluate the influence of wear and erosion it is apparent that the final selection of a material for use in die-

casting machines should not be based exclusively on these tests but should include actual service tests.

ACKNOWLEDGMENTS

The authors wish to acknowledge the contributions of Mr. R. L. Wilcox in the early stages of this work and of Mr. J. L. Rodda and others in the Research Division of The New Jersey Zinc Company.

DISCUSSION

(*D. L. Colwell presiding*)

J. C. STERN,* Aurora, Ill.—Mr. Sandell mentioned malleable iron. As I see it, malleable iron has a very thin shell of dense metal, approximately $\frac{1}{64}$ to $\frac{1}{32}$ in. thick, and machining of these parts would take off this shell and leave only the core or spongy material, which would not be satisfactory. It may be possible to cast a bushing and plunger close enough to grind the surface and not lose the hard shell. This may be worth trying; also using the casting in a hard state (that is, before annealing) and grinding to size, as the hard iron cannot be machined in any other way. The plunger tip would need to be hydrogen-brazed onto the main plunger to secure properly.

There is also chilled cast iron, which has a much deeper shell, $\frac{1}{8}$ to $\frac{3}{16}$ in. plus, which is made by pouring a good grade of cast iron into a mold that has a steel or cast-iron face coated with shellac and dusted with sand while the surface is sticky. I have found this type of material very satisfactory in dies for casting brass and bronze, and think it worth trying, as the structure is very close.

E. A. ANDERSON (author's reply).—The question has been raised as to whether we have determined the oxygen and oxide content of the cast irons used in these experiments. As I understand it, there was thought to be some possibility that the differences in penetration of the alloy along graphite streaks in the cast iron might lie in such causes. We have made no such determinations but rather feel that the use of three cast irons of the same nominal type secured from different foundries insured our obtaining a fairly representative cross section of the industry. It is to be noted that all of these cast irons behaved alike in the test.

I am inclined to believe that the explanation for the selective penetration along graphite streaks lies in the probability that an actual discontinuity exists between the graphite and the ferrite, possibly resulting from differences in thermal contraction during solidification and cooling. A case similar to this was brought out by H. L. Maxwell at a meeting of the American Society for Mechanical Engineers about two years ago. Dr. Maxwell established that molten caustic soda could penetrate along these same paths, causing leaks where the graphite streaks were continuous and substantially interconnecting throughout the cross section.

Mr. Stern has raised some interesting points with regard to two fairly common types of iron. We have not tried either malleable iron or chilled cast iron. Whether it is possible to prepare a malleable iron casting or bushing without losing the hard shell is definitely a question, as Mr. Stern points out.

* Casting Engineer, Aurora Metal Co.

A High-strength Silicon-brass Die-casting Alloy

By A. U. SEYBOLT, * JUNIOR MEMBER, AND BRUCE W. GONSER, * MEMBER A.I.M.E

(Chicago Meeting, October 1939)

A FEW copper-zinc-base alloys meet die-casting requirements reasonably well, although improvements are desired. Aluminum bronzes, high-tin bronzes and some copper-nickel-zinc alloys can be die-cast, according to Herb,¹ but seldom are because of such factors as higher melting ranges and greater cost than certain of the brasses. Fox² has summarized the copper-base die-casting alloys that were in commercial use in 1937 and has given the effects of different alloying constituents. Table 1 gives some of the properties of these alloys as reported by Fox.

TABLE 1.—*Commercial Die-casting Brasses*^a

Constituent	Yellow Brass	Low-silicon Brass	High-silicon ^b Brass	Nickel ^c Silver
Composition, Per Cent				
Cu.....	57-59	63-65	80 -81.5	42.0
Zn.....	40-42	33-35	13.5-16.0	41.0
Sn.....	0.5-1.5			
Si.....		0.75-1.25	3.75-4.25	
Pb.....				1.0
Ni.....				16.0
Properties				
Tensile, lb. per sq. in. .	55,000-60,000	65,000-70,000	85,000-95,000	85,000-95,000
Yield, lb. per sq. in. ^d	30,000-35,000	35,000-40,000	65,000-70,000	65,000-72,000
Elong., per cent in 2 in.	15-20	20-30	8-12	10-20
Brinell hardness.....	120-130	120-130	160-180	160
Specific gravity.....	8.47	8.50	8.15	8.45

^a Properties reported by Fox.²

^b Trade name of Brastil, Doehler Die Casting Co., similar to Webert Alloy,^{3,4} American Brass Co., and Tombasil Alloy,⁵ Ajax Metal Co.

^c Trade name Tinicosil, Titan Metal Manufacturing Co. Melting point (liquidus) of the yellow brass is given by Herb¹ as 1650° F., of the high-silicon Brastil (with 4.5 to 5 per cent Si) as 1600° F., and of the nickel silver as 1675° F.

^d Criterion not stated.

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* Research Metallurgist and Supervising Metallurgist, respectively, Battelle Memorial Institute, Columbus, Ohio.

¹ References are at the end of the paper.

Of particular importance are the silicon brasses, since addition of silicon is known not only to strengthen the alloy and increase its corrosion resistance but also to lower the melting point drastically, increase fluidity, diminish the tendency for zinc oxide to deposit on the die surface and permit free ejection of the casting. Unfortunately, as the silicon contents is increased the zinc content must be reduced, to avoid excessive brittleness, hence the melting range is about the same as for yellow brass, although appreciably lower than the white 16 per cent Ni brass. It was to develop an improved silicon brass that this investigation was started.

CHILL-CASTING TESTS

Tensile bar castings of about a pound weight were made in the special steel mold illustrated in Fig. 1, for the purpose of exploring a wide range

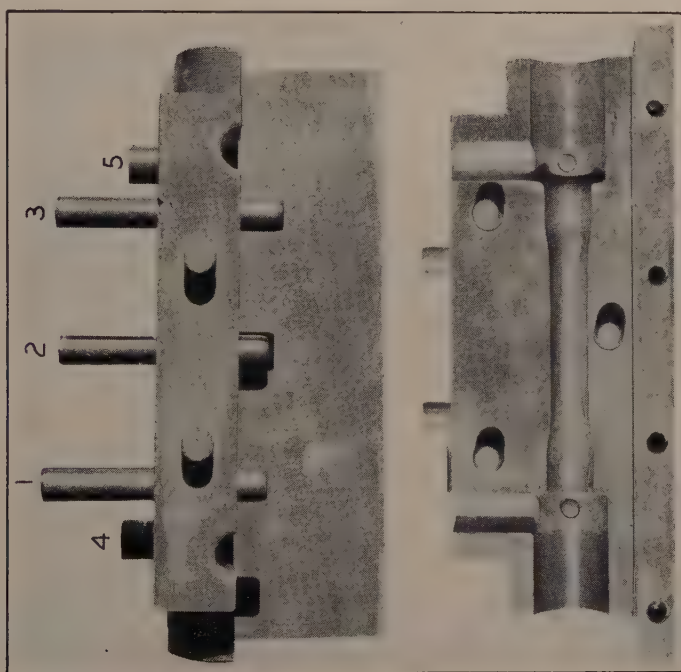


FIG. 1.—STEEL MOLD FOR MAKING CHILL-CAST TENSILE BARS.

Pegs 1, 2 and 3 serve to align the two parts of the mold, and to separate the mold after casting. Positions 4 and 5 designate ejection pins.

of compositions. This gave a standard bar of 0.505-in. diameter, as cast, with a 2-in. straight center section and $5\frac{1}{4}$ -in. over-all length.

Charges were melted in a few minutes with a small gas pot furnace. This not only gave speed but permitted detection of any tendency for any of the alloys made to be sensitive to gases from a gas-fired furnace. After melting the copper in a clay-graphite crucible under charcoal, a

copper-silicon alloy was added, then the other constituents. By this method a wide range of alloy compositions were tested quickly under

TABLE 2.—*Results of Tests on Copper-silicon-base Casting Alloys as Chill-cast*

Alloy	Composition, Per Cent	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Color	Castability and Remarks
Si Zn.....	5 Si 15 Zn	77,200	8.5	Yellow	Good
Si Sn.....	5 Si 5 Sn	68,200	0.5	Off white	Good, brittle
	5 Si 10 Sn			White	Very brittle
Si Mn.....	5 Si 2 Mn	64,700	1.0	Pale yellow	Good
Si Mg.....	5 Si 2 Mg			Gray	Good
Si Al.....	5 Si 2 Al	74,400	14.5	Yellow	Good
	5 Si 3 Al	66,400	10.0	Yellow	Very good ^d
	5 Si 4 Al	78,700	19.0	Yellow	Good ^d
	5 Si 5 Al	65,700 ^a	0	Pale yellow	Good ^d
Si Zn Sn.....	5 Si 9 Zn 1 Sn	74,400	3.5	Pale yellow	Good
	5 Si 7 Zn 3 Sn			White	Good
	5 Si 12 Zn 1 Sn	75,000	2.0	Yellow	Very good
Si Zn Mn.....	5 Si 10 Zn 2 Mn	87,300	0.5	Yellow	Good
	5 Si 10 Zn 3 Mn	68,200 ^a		Yellow	Good
	5 Si 15 Zn 3 Mn	86,700 ^a		Yellow	Good
	5 Si 6 Zn 5 Mn		2.0	Pale yellow	Good
Si Zn Al.....	5 Si 10 Zn 2 Al	61,000	0	Pale yellow	Good
	5 Si 15 Zn 2 Al			White	Good
Si Zn Mg.....	5 Si 10 Zn 2 Mg			White	Good
Si Mg Sn.....	5 Si 2 Mg 2 Sn			White	Good
Si Mn Sn.....	5 Si 5 Mn 3 Sn	69,300	0	Off white	Good
Si Mn Al.....	5 Si 4 Mn 2 Al	67,500 ^b		Yellow	Good
	5 Si 3 Mn 1 Al	84,500	1.0	Pale yellow	Good
	5 Si 2 Mn 2 Al	73,200 ^b	0	Yellow	Very good
	5 Si 1 Mn 3 Al	75,300	5.0	Yellow	Good
	5 Si 1 Mn 4 Al	90,500	2.5	Yellow	Good
Si Zn Mn Al....	5 Si 5 Zn 1 Mn 1 Al	87,000	3.0	Yellow	Good
	5 Si 10 Zn 1 Mn 1 Al	98,000	2.0	Yellow	Good
	5 Si 10 Zn 1 Mn 1 Al ⁱ	103,000	3.0	Yellow	Good
	5 Si 12 Zn 1 Mn 1 Al	95,600	3.0	Yellow	Good
	5 Si 15 Zn 1 Mn 1 Al	76,700 ^a	0	Pale yellow	Good ^h
	5 Si 10 Zn 1 Mn 2 Al	84,500 ^a		Pale yellow	Good
	5 Si 10 Zn 1 Mn $\frac{1}{2}$ Al	94,700 ^b	1.0	Yellow	Good
	5 Si 10 Zn 3 Mn 1 Al	73,700	0.5	Yellow	Good
	5 Si 10 Zn $\frac{1}{2}$ Mn 1 Al	89,600 ^b	3.5	Yellow	Good
	5 Si 10 Zn $\frac{1}{2}$ Mn $\frac{1}{2}$ Al	90,700 ^b	1.0	Yellow	Good
	5 Si 10 Zn 1 Mn 0 Al ^k	95,000	2.5	Yellow	Good
	5 Si 10 Zn 0 Mn 1 Al ^k	90,400	18.0	Yellow	Good
	5 Si 10 Zn 1 Mn 0.5 Al ^l	98,700	5.0	Yellow	Good
	5 Si 10 Zn 0.5 Mn 1 Al ^l	95,000	8.0	Yellow	Good
	5 Si 10 Zn 0 Mn 0 Al ^k	76,600	21.0	Yellow	Good
	5 $\frac{1}{2}$ Si 10 Zn 1 Mn 1 Al	88,700 ^a			
	5 $\frac{1}{4}$ Si 10 Zn 1 Mn 1 Al	90,700 ^b	1.5	Yellow	Good
	4 $\frac{3}{4}$ Si 10 Zn 1 Mn 1 Al	81,700 ^b	1.0	Yellow	Good
	4 $\frac{1}{2}$ Si 10 Zn 1 Mn 1 Al			Yellow	Good
	4 $\frac{1}{4}$ Si 10 Zn 1 Mn 1 Al	89,000	7.0	Yellow	Good
	4 Si 10 Zn 1 Mn 1 Al	87,000	3.5	Yellow	Good
	4 $\frac{1}{2}$ Si 10 Zn $\frac{1}{2}$ Mn 1 Al	60,300 ^b	2.0	Yellow	Good
	4 $\frac{1}{4}$ Si 10 Zn $\frac{1}{2}$ Mn 1 Al	82,300	12.0	Yellow	Good
	4 $\frac{1}{2}$ Si 10 Zn 1 Mn $\frac{1}{2}$ Al	76,000 ^b	2.5	Yellow	Good
	4 Si 10 Zn 1 Mn $\frac{1}{2}$ Al	73,700 ^b	4.5	Yellow	Good

^a Shoulder break due to shrinkage cracks or inclusions (usually former).

^b Faulty break due to inclusions, etc., within gauge marks.

^c Specimen cracked in two in mold, very brittle, very viscous pouring, much dross.

^d Tends to shrink-crack.

^e Cracked into fragments on cooling.

^f Cracked into fragments on cooling; much dross.

^g Good, but pitted surface.

^h Repeat test showed a white, more brittle alloy.

ⁱ Could not pour a casting without cracks.

^j Melted in coreless induction furnace.

^k This group of alloys was made subsequent to the other alloys in the table in order to show more clearly the effect of variation of the aluminum and manganese contents.

conditions approximating die-casting practice, although without exerting pressure on the casting.

Resistance to stresses involved on shrinking was qualitatively determined by the difficulty of ejection of the castings or by development of cracks at the shoulders of the button heads. Alloys that caused trouble after only a few seconds of cooling were discarded as being too brittle or having too great a shrinkage for useful service; some alloys did not crack after five minutes of cooling in the mold.

Results of Chill-cast Tests.—Tensile and casting properties of representative alloys in the field covered are given in Table 2. Freezing-range determinations were made on a few of the most promising alloys, as given in Table 3. Although the addition of 15 per cent Zn and 5 per cent Si gave the lowest freezing range of any of these die-casting brasses, alloy No. 2, with but 10 per cent Zn and 1 per cent each Al and Mn gave nearly as low a freezing range, and one that compared very favorably with the present commercial Brastil of Table 1. (The commercial alloy in present use contains 14.75 per cent Zn and 4.25 per cent Si.) Additions of metals to the copper-zinc base, other than zinc, manganese, aluminum, magnesium and tin, were excluded for various metallurgical and economic reasons. Attention was particularly directed, of course, toward lowering the freezing point. Some of the alloys tested, such as the Cu-Si-Al group, showed excellent ductility and good strength, but were discarded because of relatively high freezing ranges and cost. Magnesium was discarded because of its tendency to create an excessive amount of dross. Other alloys, such as those fairly high in tin or those beyond the yellow brass field, were too brittle to be considered useful.

TABLE 3.—*Results of Freezing-range Determinations*

No.	Composition, Per Cent					Freezing Range	
	Cu	Si	Zn	Mn	Al	Deg. C.	Deg. F.
1	80	5	15			841–825	1546–1517
2	83	5	10	1	1	852–823	1566–1513
3	88	5	5	1	1	896–852	1645–1566
4	91	5		1	3	911–886	1671–1626
5	91	5			4	918–896	1684–1644
6	90	5		1	4	920–881	1688–1617

The Cu-Zn-Si-Al-Mn alloys were early found to be the most interesting, and attention was finally turned entirely to this series. The addition of both aluminum and manganese confers definite benefits, as is indicated particularly clearly in the five alloys marked *k* in Table 2. Manganese raises the strength and lowers the ductility, while aluminum up to 1 per cent markedly increases the ductility. Hence with both elements together a suitable balance can be made between strength and ductility.

DIE-CASTING TESTS

Three silicon-brass alloys were die-cast into tensile bars at the plant of the Doehler Die Casting Co. at Batavia, N. Y., in order to compare physical properties and observe die-casting characteristics. Melts were of 200 lb. each. The die castings gave tensile bars about 9 in. long, of 0.25-in. diameter in the center, with 0.375-in. shoulders. Results of tensile tests on these bars are given in Table 4.

Each heat was cast over a range of temperature from about 1690° to 1600° F., each lot being cast at a lower temperature than the previous one.

TABLE 4.—*Tensile-test Properties of Die-cast Modified Silicon Brasses*

Casting Lot No.	Specimen No.	Tensile Strength, Lb. per Sq. In.	Yield Strength, ^a Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Brinell Hardness
Heat No. 1: 83 per cent Cu, 5 Si, 10 Zn, 1 Mn, 1 Al					
1	2	116,000	83,700	4.0	182
2	3	109,000		3.0	
3	6	112,000		5.0	
4	7	113,000		5.0	
5	10	94,500		5.0	
Heat No. 2: 83.5 per cent Cu, 5 Si, 10 Zn, 0.5 Mn, 1 Al					
1	2	99,800	76,400	6.0	163
2	3	84,700		10.0	
3	5	103,000		2.0	
4	7	104,000		6.0	
5	10	106,000		7.0	
Heat No. 3: 83.75 per cent Cu, 4.25 Si, 10 Zn, 1 Mn, 1 Al					
1	1	104,000	76,400	4	134
2	4	112,000		8	
3	6	103,000		4.5	
4	7	108,000		7.0	
5	10	110,000		4.0	

^a Determined with a standard Rhiele extensometer. Yield strength taken at 0.2 per cent offset.

No relation between the casting temperature and the physical properties were noted, however.

Many of the tensile bars, particularly those of heat No. 3, had bits of previously solidified metal (splash) embedded throughout their cross section, thus tending to lower their strength and ductility. This was not an inherent difficulty with the alloys, of course. Results reported in

Table 4 are typical of those secured from each lot, including bars with splash defects.

Comparing results of these die castings made under commercial conditions with laboratory chill castings, it is evident that casting under pressure gave generally higher mechanical properties.

From the viewpoint of the practical die-caster, the alloy used in heat No. 1 of Table 4 (83 per cent Cu, 5 Si, 10 Zn, 1 Mn, 1 Al) was considered the most desirable, as it combined high strength and high yield with adequate ductility and a low freezing range. Machinability of this alloy

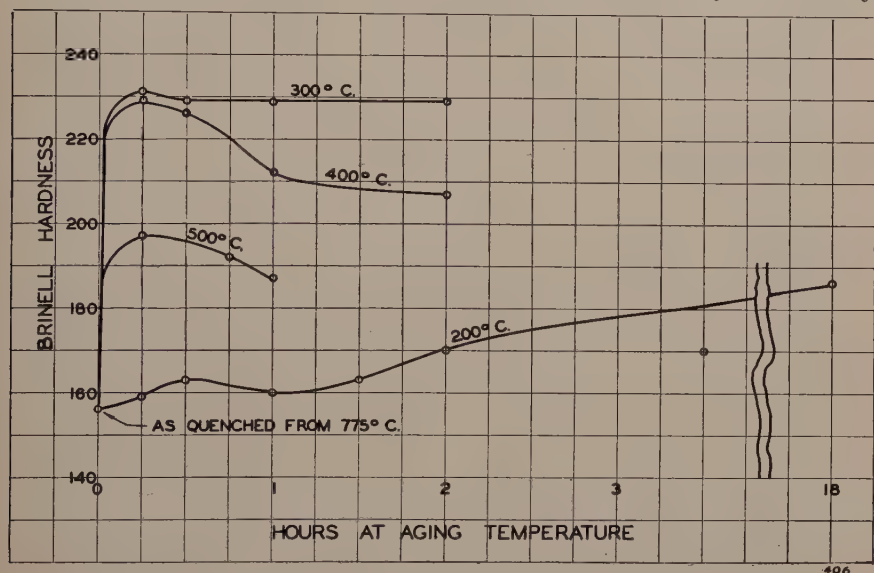


FIG. 2.—EFFECT ON HARDNESS OF AGING UNDER VARIOUS CONDITIONS.
Alloy 83 per cent Cu, 5 Si, 10 Zn, 1 Mn, 1 Al.

was considered to be practically the same as with the commercial high-silicon brass now in use (81 per cent Cu, 4.25 Si, 14.75 Zn). Surface characteristics of the modified alloys were far superior to the plain high-silicon brass, since the presence of aluminum assured a bright, smooth surface free from discoloration and scale.

PROPERTIES

Age-hardening Characteristics.—The general age-hardening characteristics of the 83 per cent Cu, 10 Zn, 5 Si, 1 Al, 1 Mn alloy were explored by water-quenching a series of chill-cast specimens after annealing for 1 hr. at 775° C. (1425° F.) and measuring the hardness after aging at various temperatures. Results are given in Fig. 2. Of particular interest in the age-hardening of these alloys is the extreme rapidity of hardening. Thus, within the experimental limits shown in Fig. 2, the maximum hardness is developed within 15 min. at 300° C. (570° F.).

Results on tensile specimens after various heat-treatments, as given in Table 5, show that overaging gives serious embrittlement and loss of strength. It is probable that the short 15-min. aging treatment at 300° C. was insufficient for the tensile specimen to reach maximum strength and hardness, since the hardness obtained was only 207 Brinell compared to 230 Brinell obtained in Fig. 2 for a much smaller specimen, which undoubtedly attained the furnace temperature more rapidly.

TABLE 5.—*Effect of Age-hardening Treatment on Tensile Properties*

Alloy 83 Per Cent Cu, 5 Si, 10 Zn, 1 Mn, 1 Al

Aging Treatment after Water Quenching	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.
As quenched (1 hr. 775° C.).....	79,000	5.5
15 min.—300° C. ^a	87,200	7.5
2 hr.—300° C.....	58,700	1.0
2 hr.—400° C.....	42,500	0.5
2 hr.—500° C.....	42,500	0.5

^a Brinell hardness of this specimen was 207.

The effect of air-cooling from a solution annealing temperature rather than quenching and reheating was investigated by making two tests. In one a chill-cast tensile bar was annealed at 800° C. (1475° F.) for an hour and air-cooled; in the other a similar specimen was annealed for 20 hours before air-cooling. Tensile strengths secured were 101,000 and 91,400 lb. per sq. in., respectively; with an elongation of 3.5 per cent in each case.

TABLE 6.—*Results of Izod Impact Tests*

Foot-pounds

Condition	Unnotched Specimens, ¼-in. Square			Notched, Standard Izod Specimens		
	Alloy 1 ^a	Alloy 2 ^a	Alloy 3 ^a	Alloy 1 ^a	Alloy 2 ^a	Alloy 3 ^a
Chill-cast.....	7	8	13.5	4	5	10
Quenched from 775° C.....	27 ^b			19	15	33
Quenched. Aged at 300° C.—15 min...	23	16	21			
Quenched. Aged at 300° C.—20 min...	21	11	28 ^b			
Quenched. Aged at 300° C.—30 min...	13	18	31 ^b	7	5.5	14.5
Quenched. Aged at 300° C.—45 min...	15	13.5	31 ^b			
Quenched. Aged at 300° C.—75 min...	17	13.5	30 ^b	5.5	5	14

^a Alloy No. 1: 83 Cu, 5 Si, 10 Zn, 1 Mn, 1 Al.

Alloy No. 2: 81 Cu, 5 Si, 12 Zn, 1 Mn, 1 Al.

Alloy No. 3: 83.75 Cu, 4.25 Si, 10 Zn, 1 Mn, 1 Al.

^b Specimens bent but did not break.

Tensile Properties at Elevated Temperatures.—No change in mechanical properties could be detected at 95° C., but at 205° and 315° C., there was a decrease in strength and elongation. At 315° C. the elongation was reduced to zero.

High-temperature Scaling.—Polished cut surfaces of the aluminum-free samples at 800° C. (1475° F.) after 19 hr. showed considerable black scale. The specimens containing 0.5 and 1.0 per cent Al were scale-free and almost bright.

Impact Tests.—Both notched and unnotched Izod tests were made on several chill-cast, high-strength, high-silicon brasses after various heat-treatments, with results shown in Table 6. No die-cast specimens were included.

METALLOGRAPHIC EXAMINATION

Structures of the quenched and die-cast specimens are similar (Figs. 3-6), and show a solid solution of the constituent elements in copper. On overaging, as shown by Figs. 4 and 5, precipitated particles become evident. Because of the complexity of the composition, no attempt has been made to define the precipitated phase or phases. There has been noted some slight indication of the presence of a precipitated phase in the die-cast sections, but it has been insufficient for resolution, even at high magnifications. Although it is probable that some precipitation takes place in die-casting, the alloy does not appear to be particularly sensitive to speed of cooling.

SAND CASTINGS

Although developed primarily for die casting, this type of alloy can be successfully sand-cast. While silicon brasses have had a rather bad reputation with the foundryman, owing to their tendency toward gas porosity, the modified silicon brasses seem less susceptible to this difficulty. As with most metals, shrinkage cavities due to inadequate feeding must be avoided by careful provision for progressive solidification.

TABLE 7.—*Mechanical Properties of Sand-cast Alloy*
Alloy 83 Per Cent Cu, 5 Si, 10 Zn, 1 Mn, 1 Al

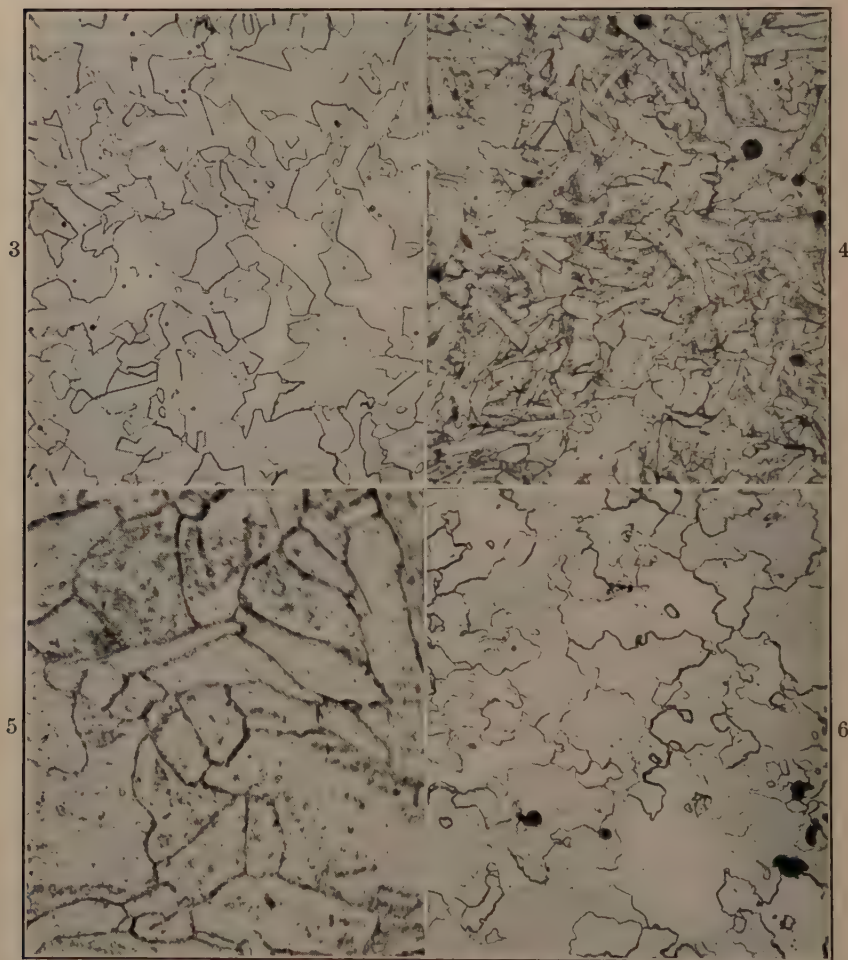
Mold and Bar No.	Tensile Strength, Lb. per Sq. In.	Yield Strength, ^c Lb. per Sq. In.	Elongation, Per Cent in 2 In.
C-1 ^a	88,000	58,500	1.0
C-2 ^a	92,000	60,000	2.5
W-1 ^b	86,500	58,500	2.5
W-2 ^b	88,000	46,500	4.0

^a Baked core sand.

^b Green sand.

^c Yield strength at 0.2 per cent offset, obtained in same manner as in Table 4.

The chief cause of porosity, dissolved gases which are expelled from the casting in the semiliquid state, is more difficult to avoid when melting is done in gas-fired furnaces, since contact between products of combustion



FIGS. 3-6.—ALLOY 83 PER CENT COPPER, 10 ZINC, 5 SILICON, 1 MANGANESE, 1 ALUMINUM.

Fig. 3. Chill-cast, reheated and quenched from 775° C. $\times 100$.

Fig. 4. Same treatment as Fig. 3 plus aging 2 hr. at 400° C. $\times 100$.

Fig. 5. Same treatment as Fig. 4. $\times 500$.

Fig. 6. Die-cast. $\times 100$.

Etched in 80 per cent ammonium hydroxide and 20 per cent hydrogen peroxide, followed by potassium dichromate solution.

and the metal is often unavoidable. Although electric melting is advantageous, melting in fuel-fired furnaces is entirely feasible. Of the products of combustion that are absorbed by the melt, hydrogen appears to be by far the most important. To eliminate this absorbed

hydrogen and make sound sand castings, the most practical means evolved has been to overheat the melt temporarily, as to about 1100° C. (2000° F.), whereby zinc vapor sweeps out most of the gas. After about one minute of this treatment the melt is quickly cooled to the pouring temperature of about 900° C. (1650° F.) and cast.

Results of tests on several tensile-bar sand castings made in accordance with the above procedure are given in Table 7.

CONCLUSIONS

1. The best high-strength die-casting copper-base alloy of those studied contains 83 per cent Cu, 5 Si, 10 Zn, 1 Mn, and 1 Al. This is on the basis of excellent physical properties and economy, combined with a low melting range. Die castings give appreciably higher values than chill castings.

2. Strength and ductility of the 5 per cent Si alloy may be varied to suit specific needs by altering the amounts of manganese and aluminum present.

3. By quenching the high-silicon brasses from 775° to 800° C. (1425° to 1470° F.), elongation and resistance to impact are improved but strength decreased. Subsequent age-hardening is very rapid, giving maximum hardness in only about 15 min. at 300° C. (575° F.).

4. These alloys containing aluminum are remarkably resistant to oxidation at high temperatures.

ACKNOWLEDGMENTS

The authors are grateful to the Union Carbide and Carbon Research Laboratories, Inc., for whom this investigation was undertaken, for permission to publish this paper. They wish particularly to thank Dr. A. B. Kinzel, of that company, for helpful counsel given throughout this work, and Mr. J. C. Fox, chief metallurgist of the Doehler Die Casting Co., whose aid in die-casting some of the alloys on a commercial scale was invaluable.

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DISCUSSION

(D. L. Colwell presiding)

C. H. SAMANS,* State College, Pa.—The authors' comment that their alloy containing 83 Cu, 5 Si, 10 Zn, 1 Mn, 1 Al gives serious embrittlement and loss of strength

* Pennsylvania State College.

on overaging seems peculiar. Generally, embrittlement of an alloy by overaging is due to a precipitate primarily in the grain boundaries, and it is then usually rather difficult to secure much change in properties by aging. Inspection of alloys 1, 2 and 3 in Table 6 suggests strongly a proximity to the alpha boundary of these alloys, and that the embrittling is caused by a transformation of appreciable amounts of the alloy to the hard, brittle beta constituent. Moreover, Fig. 4 resembles many alpha-beta two-phase structures. Have the authors examined their alloys after etching with ferric chloride or some other reagent that might make the beta phase stand out more distinctly?

Were this actually beta it might be better to sacrifice a little of the strength in order to eliminate the embrittling effects by increasing the copper content somewhat, simultaneously decreasing the silicon. The values for alloys 1 and 3 in Table 4 do not seem to differ too greatly for this to be successful.

B. W. GONSER (authors' reply).—In comparing properties of the silicon-brass die-casting alloy presented in this paper with that of 60–40 brass, it must be remembered that the addition of silicon to copper drops the melting range much more drastically than does zinc. A slightly lower freezing point is obtained with this alloy of 83 Cu, 10 Zn, 5 Si, 1 Al, 1 Mn than with 60 Cu, 40 Zn brass. Also, it is well to consider this die-casting alloy as being a silicon-copper, modified by zinc, aluminum and manganese, rather than a copper-zinc brass modified by silicon and minor constituents. In interpreting the structure, we find the copper-silicon constitutional diagram much more helpful than the copper-zinc diagram.

Pure Silicon

BY A. B. KINZEL,* MEMBER A.I.M.E., AND THOMAS R. CUNNINGHAM*

(New York Meeting, February 1939)

SILICON, unfortunately, is not in the same category as some other metals with respect to the absolute value of the highest purity material prepared. Tucker, in England, and Becket, in this country have developed procedures for the purification of silicon, and Becket's process has made industrially available silicon of a purity of 99.8 per cent or better. However, even the term "silicon metal" may be a paradox to some people, although not more so than the term "amorphous" as applied to silicon. These terms come from commerce, and "metal" is used to distinguish industrially high-purity silicon from ferrosilicon, silicon-aluminum, and other high-silicon alloys. Alloys of iron and silicon with 95 per cent Si or less are known as ferrosilicon, with a designation of silicon content where necessary, and the term "silicon metal" is invariably applied to the grades containing 96 per cent Si and higher.

The Becket method of purification was referred to in a monograph on the Alloys of Iron and Silicon, and the Tucker procedure was described in some detail in that publication.¹ In order to get silicon of still higher purity, a sample, prepared by the Becket method, analyzing 99.84 per cent Si, 0.020 Fe, 0.016 Al, 0.005 Ca, 0.025 C, 0.033 per cent O₂, 0.006 H₂, 0.006 N₂, and 0.001 per cent Mn, was crushed to pass a 100-mesh sieve and further purified by a modification of Tucker's procedure. This modification differs from Tucker's method in that after treatment the 100-mesh alloy was centrifuged to remove the last traces of acid. Our directly determined analysis of this purified sample shows: Si, 99.952 per cent; Fe, 0.009; Al, 0.012; Ca, 0.003; C, 0.006; or 99.982 per cent. Silicon by difference equals 99.97 per cent.

The variation between silicon by difference and silicon as directly determined is important. Although Tucker mentions the amount of insoluble matter in commercial silicon both before and after his treatment, he does not mention the existence of carbon in the alloy; nevertheless, he reports silicon by difference. Any final figure as to purity obviously results from agreement between direct determination and

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* Union Carbide and Carbon Research Laboratories, New York, N. Y.

¹ References are at the end of the paper.

determination by difference, and, lacking agreement, the lower value should be quoted—e.g., 99.952 per cent Si from the above.

Greiner, Marsh and Stoughton¹ emphasize that any quoted properties of silicon must be regarded as tentative, as the determinations in most cases have been made on material of lower purity than usual in such investigations. The value for density that seems to have been most generally accepted is 2.4 grams per cubic centimeter at 20°C.² However, duplicate density determinations at 20° C. using a picnometer on the 100-mesh sample of the 99.952 per cent Si product described above gave values of 2.32 each. The density determination of the 30-mesh or 40-mesh and of 80-mesh dust samples taken from the 99.84 per cent Si sample each gave the value 2.335 and the determination on the 99.84 per

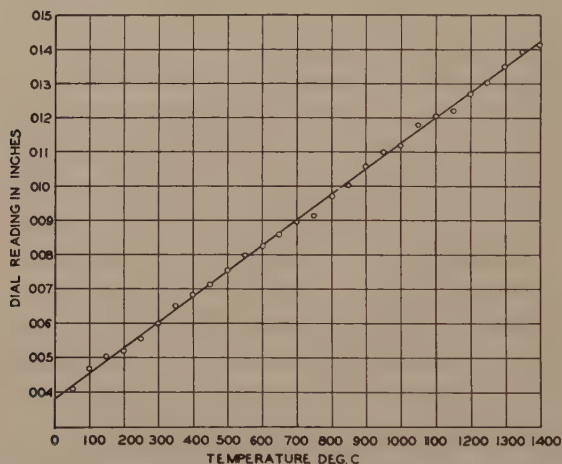


FIG. 1.—THERMAL DILATION-TEMPERATURE CURVE FOR PURE SILICON. SPECIMEN LENGTH 2.55 INCHES.

cent without screen separation gave 2.336. From this it is evident that the specific gravity of silicon of the best purity now available is between 2.32 and 2.34, and it is interesting that calculations from X-ray diffraction data indicate a value of 2.32 ± 0.02 for pure silicon.

No attempt was made to determine the melting point of the pure silicon, but attention is called to the work of Hoffman and Schulze,³ who determined 1409° C. as the melting point of 98 per cent Si, and 1411° C. as the melting point of the sample quoted as 99.89 per cent Si, and who claim an accuracy of $\pm 2^\circ$ C. for their determinations. M. L. V. Gayler⁴ reports 1415° C. $\pm 2^\circ$.

The matter of electrical conductivity of silicon is of particular interest because this is one important criterion in determining whether or not an element is a metal.⁵ In the International Critical Tables² the electrical resistivity of silicon is given as 85×10^{-3} ohm per cu. cm., or

0.085 ohm per cu. cm. This value comes from the work of Koenigsberger and Schilling.⁶ These men, who did this work carefully in every other respect, seem to have completely overlooked the matter of composition. Test rods were 2 to 6 mm. long, with a cross section of 0.3 to 0.4 sq. cm., and the authors state that these rods showed faults and pores, and they believed the absolute resistivity to be too high. The resistivity curves that covered the range of minus 190° to plus 850° C. are of particular interest in that supposedly they show the existence of three allotropic forms, alpha, beta and gamma, with transformation points at 210° and 440° C. However, they found that the higher temperature resulted in a more stable product with lower resistance. Bedel⁷ reports 0.267 ohm per cu. cm. for silicon with 0.1 per cent Fe. Bagley⁸ prepared a bar of silicon metal $\frac{1}{2}$ in. in diameter and 6 in. long. The material analyzed 96.74 per cent Si, with 0.85 per cent Fe, 0.85 per cent Ca and 1.14 Al. Resistance was measured at four intervals along the length of the bar at 18° C. The values obtained were as shown in the following table.

Interval	Ohm	Interval	Ohm
1.....	0.0329	3.....	0.0321
2.....	0.0322	4.....	0.0323
		Average.....	0.0324

The uniformity of these results indicated that the bar was sound and that a resistivity calculated from the measurements would represent the true resistivity unaffected by cracks or flaws in the material of the specimen. The resistivity calculated from these measurements was 0.0237 ohm per cu. cm. A check set of readings taken with a current three times as high as that used in the first set gave a resistivity of 0.0231 ohm per cu. cm.

Another bar was prepared from the 99.84 per cent material and the resistivity similarly measured. This gave a value of 0.08 ohm per cu. cm., which is very close to that given by Koenigsberger and Schilling,⁶ but the values along the bar varied appreciably, showing that the bar was not nearly as uniform as the bar of less pure material. It is probable that the true resistivity value of pure silicon lies between 0.02 and 0.08.

The magnetic susceptibility of silicon is given by Honda⁹ as 0.13×10^{-6} ; his silicon contained 0.085 per cent Fe. No attempt was made to get a similar figure on our material, but a qualitative test with an Alnico permanent magnet as well as with an electromagnet failed to show the slightest indication of any paramagnetic properties, which seems to show that the material is practically nonmagnetic.

Gonser and Seybolt¹⁰ obtained a dilatometric curve (Fig. 1) for the authors. They prepared a bar 2.55 in. long and 0.5 in. square cast from

99.84 per cent Si and tested it in a molybdenum-wound furnace with a hydrogen atmosphere. This curve shows continuous and regular expansion of the specimen and indicates the absence of crystallographic transformations.

In order to get some idea of the mechanical properties of the cast bar made from the 99.84 per cent material, a bar 0.254 in. square and something over 3 in. long was prepared by dint of much effort, and tested as a beam with knife-edge supports on a 3-in. span and center loading through a knife-edge. Deflection was measured directly by an indicating dial in 0.0001 in., and load measured by calibrated spring balances, using small lead shot. Using the standard formula for modulus of rupture of a rectangular beam, a value of 9046 lb. per sq. in. was obtained. A modulus of elasticity of 15,490,000 lb. per sq. in. resulted from application of the results in the standard formula, the actual breaking load of the specimen having been 35 lb., and a deflection of 0.00108 in. corresponded to a load of 12 lb. It is interesting that the load deflection plotted on cross-section paper of appropriate scale was a straight line. In this connection Templin's determination¹¹ is of interest. Working on silicon with a purity of 99.41 per cent, taken by difference, he found Young's modulus to be about 16,350,000 lb. per sq. in., based on the assumption that the value in compression is the same as in tension.

In view of the excellent corrosion resistance, low specific gravity and wide availability of silicon-containing minerals, particularly silica, the use of silicon as a structural material is a goal that has attracted the imagination of many. It remains only to produce ductile silicon, but this small remainder bids fair to be well beyond the capacity of present-day physics and metallurgy. It may be that increasing the purity of the material would lead toward some degree of malleability, but there is nothing in any of the experiments carried out to date that would indicate this to be true. It would seem that changes other than the relatively simple elimination of stranger atoms in the lattice will be necessary before ductile silicon can be produced and a wide potential field of use suitably filled. However, commercial silicon metal, nonmalleable and relatively impure from the standpoint of the physicist, is a much valued and important article of industry. This is available in several grades, 96, 97 and 98 per cent minimum silicon being normally specified, depending upon the application. Iron is the impurity generally given the most importance, and the grades mentioned above will contain slightly less than 2, 1 and 0.5 per cent iron, respectively. Aluminum and calcium practically account for the remainder. As this silicon is used primarily in the production of silicon-aluminum and silicon-copper alloys, there has been very little immediate industrial need for elimination of the elements other than iron.

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DISCUSSION

(E. E. Schumacher presiding)

R. VINES,* Bayonne, N. J.—Has any attempt been made to produce pure silicon by the thermal decomposition of a volatile silicon compound, such as silane or one of the silicon halogen compounds, using a method similar to that developed by de Boer and Fast for zirconium? In this method zirconium iodide, formed from crude zirconium and a small amount of iodine, is decomposed on a heated wire, yielding relatively pure metal. Similar methods have been used with tungsten and titanium.

A. B. KINZEL (authors' reply).—Silicon has been deposited on other metals by decomposition of the tetrachloride. It has been deposited on a carbon filament under similar conditions. R. Holbling¹² reports the preparation of a bar of silicon 4 mm. thick by deposition on such filament at 1000°C. Other volatile compounds of silicon have been used for the same purpose on a purely experimental basis. While these methods are interesting from the experimental standpoint, they have never passed the purely test-tube stage.

* Research Laboratory, International Nickel Co.

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Tensile Properties of Rolled Magnesium Alloys, I—Binary Alloys with Aluminum, Antimony, Bismuth, Cadmium, Copper, Lead, Nickel, Silver, Thallium, Tin and Zinc

BY JOHN C. McDONALD,* JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

THE amount of published literature in the field of mechanical properties of magnesium alloys is not great; particularly with respect to rolled alloys. Houghton and Prytherch¹ have summarized most of the articles to 1937, including their own work on sheet. Although many papers can be found dealing with the technology of magnesium and the alloys now in commercial use, there does not seem to be any work dealing exclusively with the variation in properties of rolled alloys as caused by changes in alloy composition. Comparison of published data reveals considerable discrepancies in properties of alloys of the same composition, probably due to differences in the details of working and heat-treating followed by different workers. The purpose of this paper is to study the properties of alloys in conditions where the effects of such differences have been eliminated.

It is well known that the strength and ductility of metals are functions of the working and heat-treating they have received, as well as of their chemical composition. In comparing alloys with respect to these properties, therefore, all possible combinations of the variables of the fabrication procedure ought to be carried out on each alloy. One or more of these treatments will produce the highest ductility, or strength, or both. These highest properties would then be selected as characteristic of each alloy, and alloys would be compared on the basis of those properties. Thus a separation of the effect of composition and that of working and heat-treating would be achieved. In this paper, however, a compromise with completeness has been made by carrying out a restricted number of treatments. As a consequence, the properties obtained are not necessarily the best that the alloy is capable of exhibiting; but since all alloys have been treated by the same method, the results ought to be comparable.

The elements selected for the study comprise a class that will alloy easily with magnesium, and that are relatively cheap. Each was added in different amounts, up to a limit that varied with the element.

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* The Dow Chemical Co., Midland, Mich.

¹ References are at the end of the paper.

PROCEDURE

The alloys were made by melting the magnesium under a commercial flux and adding the alloying metal. The magnesium was of commercial purity, about 99.95 per cent, and the alloying elements were also of commercial grade, 99 per cent pure or better. No effects appeared that could be attributed to impurities. Each alloy was cast by ladling the metal into a cylindrical steel mold (diameter, 4 in.) to a depth of 6 in., giving a billet weighing approximately 5 lb. The billet surface was then machined smooth on a lathe.

The machined billet was preheated for about 12 hr. at 600° F. before being extruded into 2.0 by 0.14-in. bar from a container at the same temperature. This preheat was sufficient to permit each alloy studied to be extruded at a reasonable pressure, which in every case was adjusted to give maximum extrusion speed without producing hot-shortness.

The bar was cut up into 6-in. lengths, a piece from the center being analyzed. Spectrographic analysis was used for aluminum, zinc, and, in part, for cadmium; the others were analyzed by chemical means.

The bars were preheated 15 min. at a controlled temperature and given one pass in the mill, after which they were replaced in the furnace for 15 min. of reheating and annealing. This procedure was repeated, at the same reduction per pass, until about 50 per cent total reduction had been achieved. The mill was a cold strip mill with polished rolls 3 in. in diameter by 3-in. face; it was powered by a 5-hp. motor and operated at 80 ft. per min. Preliminary test rolling was carried on in the range of temperatures 400° to 800° F., and in the range of reduction per pass, 10 to 30 per cent. This established the limits of hot-shortness and cold-shortness for each alloy.* However, reductions as high as 30 per cent were not used often because of power limitations. Finally, 12 pieces of each alloy were rolled at a temperature and reduction per pass somewhat above the cold-short limit. Such specimens were hard enough so that annealing was required to develop the maximum ductility.† In some alloys, the hot-short and cold-short limits approached very closely, making the alloys completely unrollable.

The ideal way to be sure of developing maximum ductility would be to anneal these hot-rolled pieces at 50° intervals in the range of 300° to

* Magnesium and its alloys cannot be rolled indefinitely below a certain temperature limit without cracking. Below this temperature limit, the percentage of total reduction at which cracking begins depends both on the percentage of reduction per pass and on the temperature. The term "cold-shortness," refers to this cracking, and the phrase "cold-short limit" means a combination of temperature and reduction per pass at which cracking just begins when 50 per cent total reduction is reached.

† Extensive preliminary experiments showed that metal hot-rolled near the cold-short limit for a total reduction of 50 per cent was fairly hard and extremely fine-

900° F., since, as a recent paper² shows, the recovery temperature, or range of temperatures, varies widely for different magnesium alloys. However, a compromise between completeness and a practicable amount of work per alloy was reached by annealing five specimens 30 min. each, at 400°, 500°, 600°, 700°, and 800° F., respectively. To get a rough idea of the age-hardening characteristics of each alloy, three more specimens were annealed 16 hr. at 350° F., after the 30-min. treatment at 600°, 700°, and 800° F. Preliminary experiments, including X-ray study of solid solubility, demonstrated that this solution time was sufficient for substantial equilibrium; in aluminum alloys, at least.

Three specimens were cold-rolled 2.5, 5, and 10 per cent, respectively, at around 0.5 per cent per pass; one of these would usually develop the maximum strength of which the alloy was capable. The twelfth piece was tested in the hot-rolled condition.

The specimens, now 2 by 12 in., were cut into two 6-in. lengths and one of these halves was cut lengthwise to give two 6 by 1-in. test blanks per treatment. This left 6 in. of specimen for any further work desired. A standard A.S.T.M. reduced section was cut into blank with a milling cutter. Each bar was then pulled in tension at a speed of around 0.25 in. per minute on an Amsler machine. The stress-strain curves for a sufficient number of bars were determined, that a graph of load at 1 per cent elongation versus 0.2 per cent yield stress could be drawn. Yield stress was subsequently determined by making but the one measurement at 1 per cent elongation. Other workers³ have shown that testing speed can affect properties; but since the speed was kept the same for all specimens, the data will still be comparable. Strengths were calculated on the original cross section. Percentage elongation was measured over a 2-in. gauge length. The average of the two bars was the value finally taken.

The highest percentage of elongation obtained by annealing was selected as representative of the maximum ductility of the alloy. The properties of the specimen with this elongation are designated by the word "soft" in the figures. If more than one specimen had this highest percentage of elongation, properties of the one with the highest yield stress were selected.

The highest yield strength produced by cold-rolling was selected as representative of the maximum strength the alloy could develop; in the figures the properties of the specimen with that strength are designated by the word "hard."

grained. Annealing of this metal caused grain growth and softening, until, as the temperature of anneal was increased, a maximum in ductility was reached; at higher temperatures, further softening, and a decrease in ductility, was observed.

These results are similar to those of Haughton and Prytherch,¹ except that they varied the rolling temperature and measured properties in the hot-rolled state.

Before plotting the properties against percentage composition, the data, originally calculated to three places, were rounded off. Smooth curves were then drawn among the plotted points, so that a graphical averaging over composition was obtained. The final results are taken from the curves, thus reducing the error due to the scatter of the points. Undoubtedly a greater number of treatments per alloy would have eliminated a good deal of the scatter. The rest must be attributed to inability to control the working conditions closely enough.

The percentage elongation of the specimens of maximum strength was not plotted. It was always very low (1 to 7 per cent); in addition, its variation with percentage composition was not significant.

No attempt was made to study properties in any direction other than that of rolling, because of the narrowness (2 in.) of the specimens. In two cases, the properties were so poor that the results are presented only in tabular form.

ALLOYS STUDIED

Magnesium-aluminum Alloys.—The properties of alloys of this system are presented in Fig. 1. From these curves we can select the best alloys of the system from the standpoints of highest ductility, highest strength, and the best combination of these two properties. Table 1 presents the properties of the alloys so chosen, both in the annealed and in the cold-rolled condition. Comparison of these results with those of Haughton and Prytherch,¹ Haughton and Tate,⁴ and

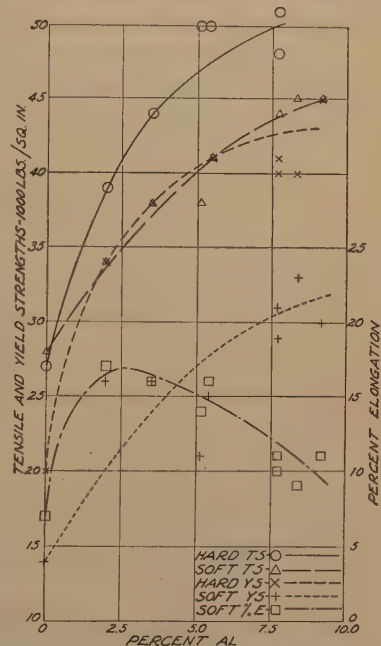


FIG. 1.—PROPERTIES OF MAGNESIUM-ALUMINUM ALLOYS. Hard = cold-rolled; soft = annealed.

TABLE 1.—Properties of the Best Alloys of the Magnesium-aluminum System

Property	Ductility, 3 Per Cent Al		Strength, 9 Per Cent Al		Both, 6 Per Cent Al	
	Annealed	Cold-rolled	Annealed	Cold-rolled	Annealed	Cold-rolled
Elongation, per cent.....	16		10		14	
Yield strength, 1000 lb. per sq. in.....	23	37	30	43	28	41
Tensile strength, 1000 lb. per sq. in.....	36	42	45	50	42	48

Broniewski, Bernaciak, and Blazewski⁵ emphasizes the point previously made that while agreement among workers is sometimes good, it is also sometimes not so good; therefore, no numerical comparisons will be made here. On the whole, the agreement in properties may be said to be fair.

Age-hardening was observed in all except the two lowest alloys; i.e., from somewhere around 4 or 5 per cent on up. This figure is in agreement with other workers, Chubb⁶ states in his recent review. The greatest strengths were produced by cold-rolling.

The extruded bar was smooth in appearance, whereas the unalloyed magnesium is rough, probably because of the much larger grain size as cast of the pure metal. The percentage of added aluminum was always

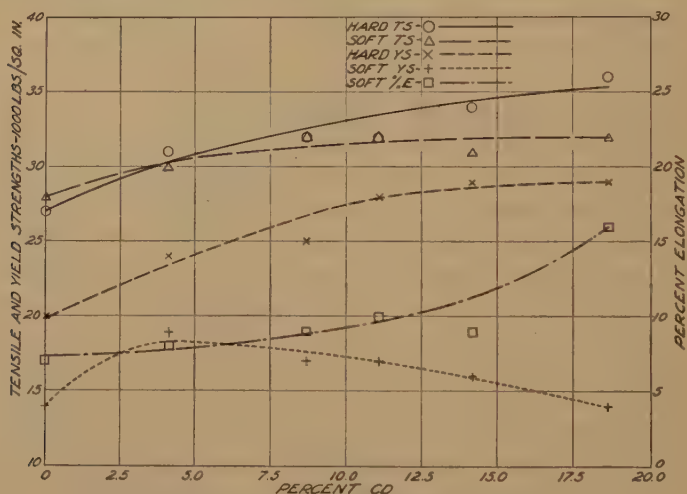


FIG. 2.—PROPERTIES OF MAGNESIUM-CADMIUM ALLOYS.
Hard = cold-rolled; soft = annealed.

more than that required to produce refinement in castings according to Hanemann and Hoffman.⁷

As the amount of second phase present at room temperature increased, the cold-short temperature limit also increased. The hot-short temperature limit above 6 per cent Al was well under the eutectic temperature of 817° F. The presence of impurities that would produce a lower melting eutectic does not seem an adequate explanation for the effect. Rather, it must be due to a loss in cohesiveness of the alloy, which increases as the solidus temperature is approached. Hot-shortness under 800° F. could not be observed below 7 per cent Al. Above this percentage, not even prolonged solution heat-treatments would remove it. Possibly the local heat generated by the working is sufficient to raise the temperature above the solidus, which would certainly result in low cohesiveness.

Magnesium-antimony Alloys.—Magnesium-antimony alloys had a very rough appearance as extruded, and had to be rolled at a high temperature. A few tenths per cent of antimony seems to be of some benefit, in agreement with Peredelski,⁸ but more than this produces too much brittleness to make the element of any value for sheet alloys. Table 2 gives the actual properties. No age-hardening was observable, in accordance with the published phase diagrams (Haughton and Prytherch¹). Cold-rolling increased the yield strength without materially affecting the tensile strength.

Magnesium-bismuth Alloys.—Almost the same remarks may be made about bismuth as about antimony. Alloys of above 2 per cent Bi, however, could not be cold-rolled at all. Table 3 gives the properties, which indicate a slight superiority of bismuth over antimony.

Magnesium-cadmium Alloys.—These alloys also had a rough appearance at the lower percentages as extruded. No age-hardening was producible (as would be expected from the phase diagram). Fig. 2 presents the data graphically.

The agreement with Haughton and Prytherch¹ is fair. It would be difficult to choose an alloy of "best" combination of properties, since

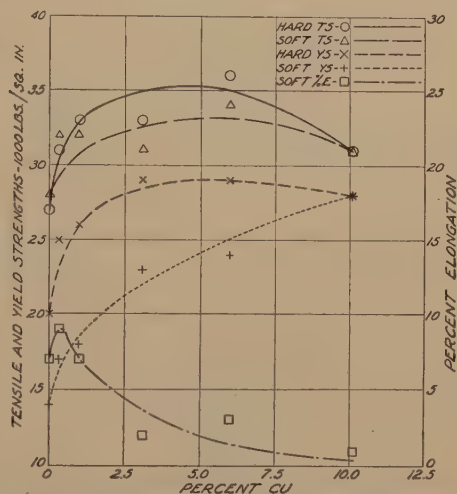


FIG. 3.—PROPERTIES OF MAGNESIUM-COPPER ALLOYS.

Hard = cold-rolled; soft = annealed.

TABLE 2.—Properties of Magnesium-antimony Alloys

Sb, Per Cent	Elongation, Per Cent		Yield Strength, 1000 Lb. per Sq. In.		Tensile Strength, 1000 Lb. per Sq. In.	
	Annealed	Cold-rolled	Annealed	Cold-rolled	Annealed	Cold-rolled
0.1	3	1	19	27	30	32
3.0	2	1	18	25	26	25
5.4	1	1	22	26	28	29
7.3	1	1	25	28	27	28

the figure shows that in the annealed state, as ductility goes up, yield strength goes down. In the cold-rolled state, greatest strength is developed at the maximum percentage studied.

Magnesium-copper Alloys.—These alloys had a smooth surface as extruded, and rolled well. Fig. 3 presents the data. The curves show two best alloys, whose properties are given in Table 4.

Above 5 per cent, the hot-rolling temperature had to be raised; at 10 per cent the alloy was too brittle to be cold-rolled. This brittleness checks with the findings of Cook and Jones,⁹ but the property agreement with their values for forgings is general only. No age-hardening was detected, in agreement with their results, and the phase diagram as published.

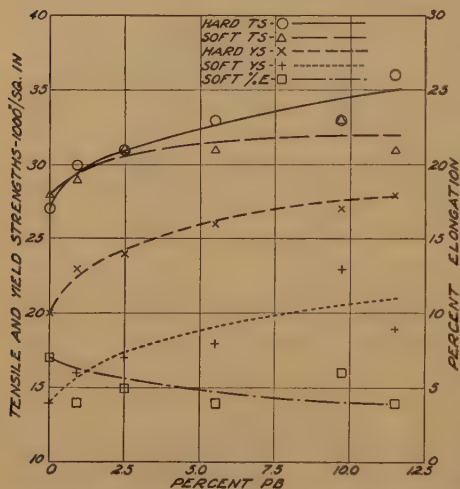


FIG. 4.—PROPERTIES OF MAGNESIUM-LEAD ALLOYS.

Hard = cold-rolled; soft = annealed.

The best alloys in the range studied are given in Table 5.

Magnesium-silver Alloys.—These alloys were annealed at 450° to 850° F., and age-hardened at 400° F., as it was thought that these con-

Magnesium-lead Alloys.—Fig. 4 shows that lead produces some strengthening, with slight loss in ductility. The surface of the extruded metal was rough, and a high rolling temperature was necessary. No age-hardening was observed.

Magnesium-nickel Alloys.—Magnesium-nickel alloys are similar to copper in many respects, but the properties are better. No age-hardening is observed; the high alloys require a higher rolling temperature, and become brittle. Fig. 5 presents the data.

TABLE 3.—Properties of Magnesium-bismuth Alloys

Bi, Per Cent	Elongation, Per Cent		Yield Strength, 1000 Lb. per Sq. In.		Tensile Strength, 1000 Lb. per Sq. In.	
	Annealed	Cold-rolled	Annealed	Cold-rolled	Annealed	Cold-rolled
0.2	4	2	20	27	30	32
0.6	3	2	21	24	31	31
2.0	3	2	22	26	32	32
6.3	3		23		32	
9.0	3		24		34	

ditions would be more favorable for age-hardening than those used for the alloys with other elements. Despite this, no age-hardening was observed, for an unascertained reason. Fig. 6 shows that silver produces

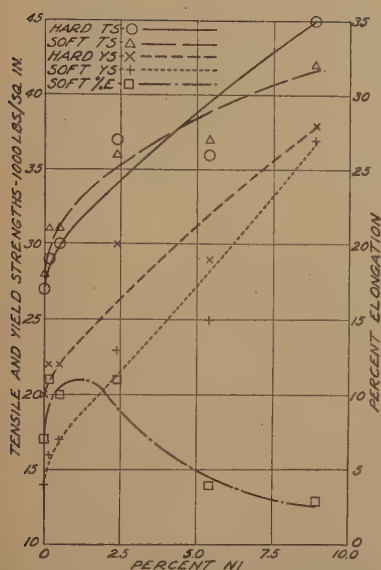


FIG. 5.—PROPERTIES OF MAGNESIUM-NICKEL ALLOYS.

Hard = cold-rolled; soft = annealed.

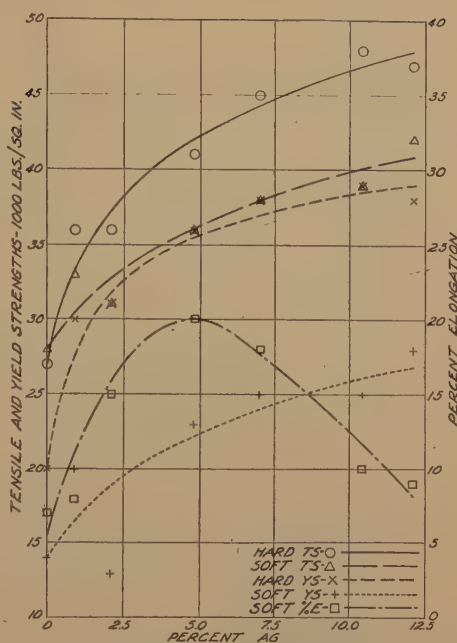


FIG. 6.—PROPERTIES OF MAGNESIUM-SILVER ALLOYS.

TABLE 4.—Properties of the Best Alloys of the Magnesium-copper System

Property	Ductility, 0.3 Per Cent Cu		Strength, 5 Per Cent Cu	
	Annealed	Cold-rolled	Annealed	Cold-rolled
Elongation, per cent.....	9		2	
Yield strength, 1000 lb. per sq. in.....	16	23	24	29
Tensile strength, 1000 lb. per sq. in.....	29	31	34	35

TABLE 5.—Properties of the Best Alloys of the Magnesium-nickel System

Properties	Ductility, 1.5 Per Cent Ni		Strength, 9 Per Cent Ni	
	Annealed	Cold-rolled	Annealed	Cold-rolled
Elongation, per cent.....	11		3	
Yield strength, 1000 lb. per sq. in.....	19	25	37	38
Tensile strength, 1000 lb. per sq. in.....	34	32	42	45

good properties when added to magnesium. The best alloys are given in Table 6.

Magnesium-thallium Alloys.—Fig. 7 shows these alloys to be weak, but ductile. The extruded bar is rough at the lower percentages. Thallium is like cadmium in that ductility rises while strength falls. The increase in ductility is greater, and the loss in strength less, however.

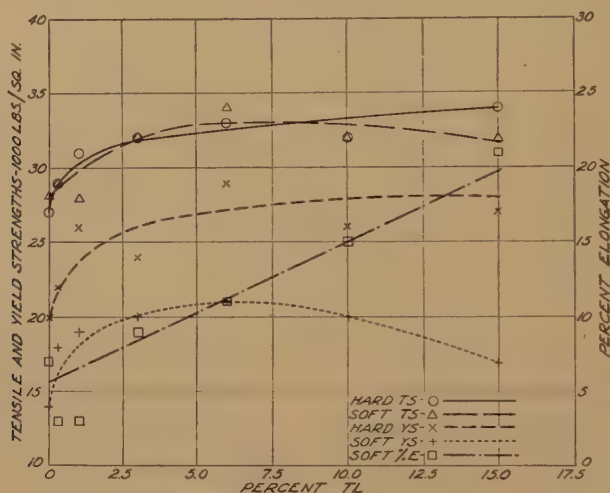


FIG. 7.—PROPERTIES OF MAGNESIUM-THALLIUM ALLOYS.
Hard = cold-rolled; soft = annealed.

Magnesium-tin Alloys.—Fig. 8 shows that tin strengthens magnesium considerably, with some loss in ductility. The extruded bars were rough, and had to be rolled at a high temperature. Because of the nature of the phase diagram, annealing was done at 400°, 500°, 600°, 800°, and 1000° F.; age-hardening was at 450° F. Hardening was observed from 4 per cent Sn on up.

TABLE 6.—Properties of the Best Alloys of the Magnesium-silver System

Properties	Ductility, 4 per cent Ag		Strength, 12 per cent Ag		Both, 8 per cent Ag	
	An- nealed	Cold Rolled	An- nealed	Cold Rolled	An- nealed	Cold Rolled
Elongation, per cent.....	20		9		16	
Yield strength, 1000 lb. per sq. in.....	22	35	27	39	25	38
Tensile strength, 1000 lb. per sq. in.....	35	41	41	48	39	45

Magnesium-zinc Alloys.—The rolling temperature of these alloys was lower than that of the others, correlating with the lower eutectic melting

point (644° F.). Again the phenomenon was observed of hot-shortness in solution heat-treated single-phase alloys at temperatures well below that of the eutectic melting point. Fig. 9 presents the data in the usual form. The ductility of 2 per cent Zn is less than that reported by Haughton and Prytherch.¹ Note how closely the yield strength, in the cold-rolled state, and tensile strength, in the

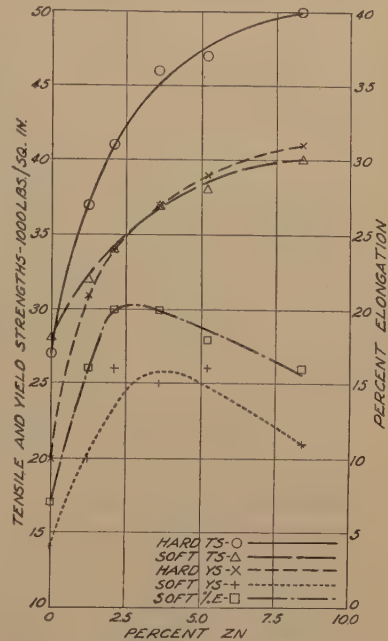
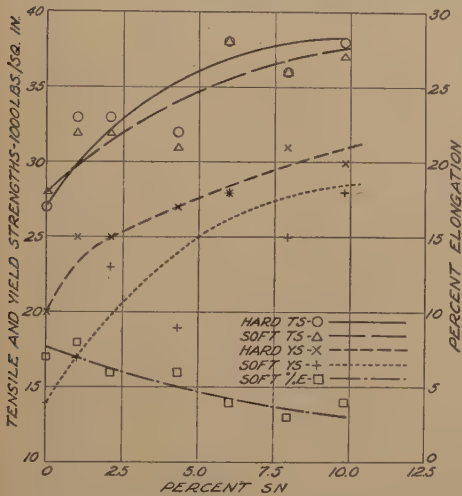


FIG. 8.—PROPERTIES OF MAGNESIUM-TIN ALLOYS. FIG. 9.—PROPERTIES OF MAGNESIUM-ZINC ALLOYS.

Hard = cold-rolled; soft = annealed.

annealed state, agree. This phenomenon can be seen on many of the graphs. The best alloys in the range studied are given in Table 7.

Age-hardening was observed from 2 per cent Zn up. This makes the 5 per cent Zn alloy additionally desirable, since it can be age-hardened considerably.

TABLE 7.—Properties of Best Magnesium-zinc Alloys in Range Studied

Properties	Ductility, 3 Per Cent Zn		Strength, 8 Per Cent Zn		Both, 5 Per Cent Zn	
	Annealed	Cold-rolled	Annealed	Cold-rolled	Annealed	Cold-rolled
Elongation, per cent.....	20		16		19	
Yield strength, 1000 lb. per sq. in.....	26	36	21	41	25	39
Tensile strength, 1000 lb. per sq. in.....	36	44	40	50	38	47

CONCLUSIONS

We are now in a position to compare these binary alloys to see which are the best in the classifications we have made. The best ones are: for ductility, 3 per cent Zn; for strength, 9 per cent Al; and for both, 6 per cent Al, where strength is the primary object; and 5 per cent Zn, where ductility is the primary object. If the sheet may be age-hardened to attain strength, 5 per cent Zn offers the best combination. Thus, the superiority of aluminum and zinc alloys is established. Alloys of silver are also good, but are somewhat inferior to the best alloys just mentioned.

The alloying elements can be divided into classes according to the nature of their effect:

1. Strengthening increases continuously with alloy content to a possible maximum, but ductility has a maximum at a lower alloy content than the maximum in strength. In order of their effectiveness, we have: for strength, aluminum, zinc, silver, nickel, copper; for ductility, zinc, silver, aluminum, nickel, and copper.
2. Little strengthening, but increased ductility: thallium and cadmium.
3. Strengthening, but loss in ductility: tin, lead, bismuth, and antimony.

Another way of summarizing the results would be to classify the metals according to the sum total of observed effects and the desirability on that basis of using those elements in sheet:

1. Highly desirable: zinc, aluminum, silver, thallium, and cadmium.
2. Possibly desirable: nickel and copper.
3. Not desirable: tin, lead, bismuth, and antimony.

It must be recognized that the properties of polynary alloys of magnesium with these elements are not predictable solely on the basis of the properties of the binary alloys. However, the effect of the added metal in binary combination does furnish a lead as to where the emphasis should be put in studying polynary alloys.

SUMMARY

1. The tensile properties of several magnesium-base binary alloys have been studied in rolled strips by a method adopted especially to eliminate comparisons in which the effects of working would play a part; rather, the results are comparable strictly on a basis of alloy composition.
2. The following elements have been studied up to the limits indicated: 9 per cent Al, 7 per cent Sb, 9 per cent Bi, 18 per cent Cd, 10 per cent Cu, 11 per cent Pb, 9 per cent Ni, 12 per cent Ag, 15 per cent Tl, 10 per cent Sn, 8 per cent Zn.
3. These elements may be arranged in order of the goodness of their general effect as follows: zinc, aluminum, silver, thallium, cadmium, nickel, copper, tin, lead, bismuth, and antimony.

ACKNOWLEDGMENTS

The author wishes to express his thanks to The Dow Chemical Co. for permission to publish these results; to Dr. J. D. Hanawalt, for his suggestions and criticism; to Mr. H. A. Diehl, for assistance in various phases of the work; and to all those who have helped by their criticism in the writing of this paper.

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An X-ray Study of the Alloys of Silver with Lead, Bismuth and Thallium

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(New York Meeting, February 1940)

IN recent years considerable attention has been devoted to the development of new commercial uses for silver, chiefly because of lowered prices and large stocks of the metal. This has led to increased interest in the phase diagrams of silver alloys. The silver-lead diagram is reported¹ to be of the simple eutectic type, but no measurements of the solubility of lead in silver have been made. The solubility of silver in lead has been estimated² from diffusion experiments and resistance measurements to vary with temperature from 0.09 to 0.18 atomic per cent (0.05 to 0.10 weight per cent). Silver-rich silver-lead alloys have recently been recommended as high-strength bearing metals.³ The silver-bismuth diagram is similar.¹ The solubility of bismuth in silver has been estimated to be about 5.5 weight per cent on the basis of X-ray work.⁴ Matthiessen⁵ found a solubility of silver in bismuth from 0.25 to 0.50 per cent by conductivity measurements. Silver and thallium form the same type of diagram,¹ with no data on their mutual miscibilities.

We have studied the first two of these diagrams by X-ray methods, verifying their main features and determining the solubilities of lead and bismuth in silver at several temperatures. We also determined the solubility of thallium in silver at one temperature. The solubilities of silver in lead and in bismuth were found to be too low to be detectable.

MATERIALS AND METHODS

Mallinckrodt precipitated silver, analytical reagent, was used. Maximum impurities listed on the label were: chloride, 0.005 per cent; copper, 0.001; iron, 0.002; other heavy metals (as Pb), 0.002; and sulphate (SO_3), 0.05. The lattice constant was found to be $a_0 = 4.0782 \text{ \AA.}$, in good agreement with the value of Jette and Foote,⁶ $a_0 = 4.0779 \text{ \AA.}$, for

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¹ References are at the end of the paper.

pure silver. Spectrographic standard lead was purchased from the American Smelting and Refining Co., known impurities being stated as less than 0.0001 per cent. Its lattice constant was found to be $a_0 = 4.9399$, compared with $a_0 = 4.9396$ listed by Wyckoff⁷ for pure lead. Mallinckrodt's analytical reagent bismuth was used. The follow-

 TABLE 1.—*Silver-lead Alloys*

Weight Per Cent Lead	Temperature of Anneal, Deg. C.	Lattice Constant, Å.	Solubility of Lead, Weight Per Cent
0.0		4.0782	a
0.5	300	4.0804	a
1.0	300	4.0823	a
2.0	300	4.0835	1.3
3.0	300	4.0835	1.3
4.0	300	4.0837	1.3
25.0	300	4.0837	1.3
25.0	280	4.0826	1.0
25.0	250	4.0807	0.6

^a One-phase region.

ing maximum impurities were listed on the label: arsenic, 0.000 per cent; copper, 0.005; iron, 0.00; lead, 0.00; silver, 0.005; zinc, 0.00. Its lattice constants were found to be $a_0 = 4.5367$, $c_0 = 11.8381$, compared with the values of Jette and Foote,⁶ $a_0 = 4.5372$, $c_0 = 11.8381$, for pure bismuth.

 TABLE 2.—*Silver-bismuth Alloys*

Weight Per Cent Bismuth	Temperature of Anneal, Deg. C.	Lattice Constant, Å.	Solubility of Bismuth, Weight Per Cent
0.0		4.0782	a
0.5	259	4.0805	a
0.6	259	4.0809	a
1.0	259	4.0832	a
3.0	259	4.0853	1.5
25.0	259	4.0852	1.5
1.0	250	4.0833	a
1.0	226	4.0822	0.8
2.0	226	4.0824	0.9
1.0	200	4.0812	0.6
2.0	200	4.0813	0.6

^a One-phase region.

Thallium was obtained from A. D. Mackay, New York, and was said to be more than 99 per cent pure. Its lattice constant was not determined.

Alloys were prepared by melting the metals together to form ingots weighing 1 to 2 grams. The melting was done in evacuated, sealed-off Vitreosil tubes by holding the tubes for 5 min. in a furnace at 1010°C.

TABLE 3.—*Silver-thallium Alloys*

Weight Per Cent Thallium	Temperature of Anneal, Deg. C.	Lattice Constant, Å.	Solubility of Thallium, Weight Per Cent
0.0		4.0782	a
0.5	287	4.0793	a
1.0	287	4.0804	a
2.0	287	4.0832	a
4.0	287	4.0884	a
25.0	287	4.1023	9

a One-phase region.

Ingots of which the loss in weight was less than 0.1 per cent were accepted without analysis; all others were rejected. The ingots were cold-worked and annealed in a vacuum for four weeks at a temperature 10°C. below the eutectic temperature, in order to secure maximum homogeneity. Powders filed from these ingots were sealed off in evacuated Pyrex tubes and given a final anneal for several weeks at temperatures held constant within 1°C., finally being quenched by suddenly breaking the tube under water.⁸ Lattice constants corrected to 25°C. were determined by Cohen's^{9,6} method, using a back-reflection focusing camera. To ensure equilibrium, each determination made after an anneal of two weeks was repeated with an anneal of four weeks. Checking results were obtained in each case.

RESULTS

The absence of intermediate phases in the silver-lead and silver-bismuth systems was confirmed. Powder patterns of samples of intermediate composition annealed for four weeks near the eutectic temperature showed the presence of two phases, which were identified as the terminal solid solutions. Diffraction patterns of the thallium phase were not obtained, probably because of tarnishing difficulties.

The lead phase showed no change of lattice constant in the presence of silver. If Vegard's law were followed, a silver solubility of 0.06 atomic per cent (0.03 weight per cent) could be detected. The bismuth lattice constants changed less than the estimated experimental error (1 part in 10,000), when melted and annealed with silver, consequently the solubility of silver in bismuth must also be small. Solid solubilities of silver-rich alloys were determined by the method shown in Fig. 1. Results are given in the tables. The thallium solubility was not as accurately determined as the others because of a long extrapolation complicated by a slight curvature in the lattice constant-composition curve. Temperature versus solubility for the silver-lead and silver-bismuth systems are plotted in Figs. 2 and 3.

DISCUSSION OF RESULTS

The solubility of lead in silver was found to be much less than the value estimated by Hansen;¹ moreover, it decreases rapidly with tempera-

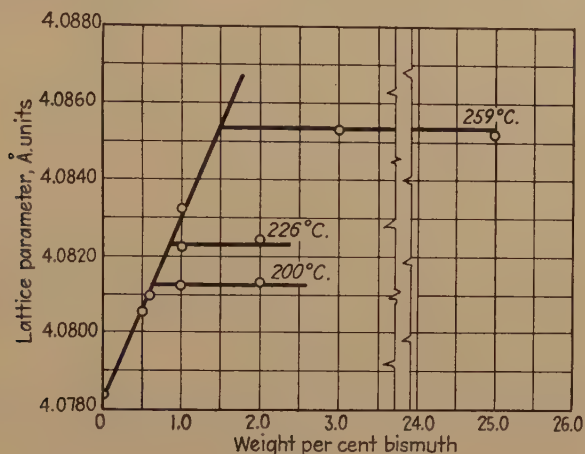


FIG. 1.

ture, a fact that he did not show in his diagram. The solubility of bismuth in silver is far less than that found by Broderick and Ehret⁴ by X-ray methods for "slowly cooled" alloys. The difference in results lies mainly in the lattice constant-composition curve for the one-phase

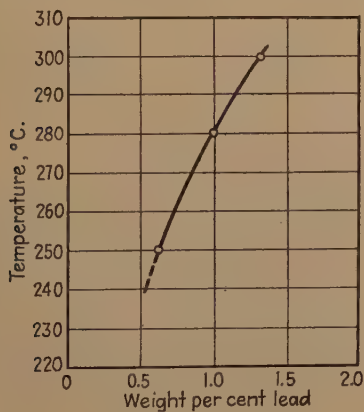


FIG. 2.

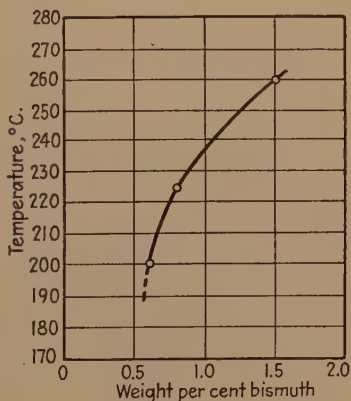


FIG. 3.

region. The rather remarkable shape of their curve could be explained by precipitation of bismuth during cooling. Since their work was performed at a time when the importance of constant-temperature annealing and rapid quenching was often not appreciated, we feel that this is a probable explanation.

There is a small negative deviation from Vegard's law in the lead and bismuth systems; a considerable one for thallium. Lead and bismuth atoms have a much larger radius than silver (21 and 26 per cent, respectively) so that, according to Hume-Rothery,¹⁰ their miscibility should be severely restricted by the size factor and should decrease with temperature. Our results bear out these predictions. Thallium, with a size factor nearly as unfavorable (19 per cent larger than silver), has a solubility of nearly 5 atomic per cent. Probably this can be accounted for by an attraction between thallium and silver atoms, which is indicated by the negative deviation from Vegard's law.

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Effect of Composition upon Physical and Chemical Properties of 10-karat Gold Alloys

By TRACY C. JARRETT,* JUNIOR MEMBER A.I.M.E.

(Chicago Meeting, October 1939)

IN making gold alloys possessing certain physical properties, such important factors as corrosion resistance, color, hardness and melting points must be considered. All of these requirements depend directly upon the composition. It is possible to obtain the same colored gold alloy by using different compositions, but in doing so one may bring in some undesirable property. Other investigations have been carried on in this field by F. E. Carter,¹ E. M. Wise,² and L. Sterner-Rainer.³

To make a complete study of the effect of composition upon these properties, a systematic investigation was carried on involving a range of copper content from 85 to 65 per cent. Elements such as zinc, silver and nickel were used to replace in part the copper content. The gold content in all the alloys remained constant.

Only 10-karat gold alloys of those containing 41.6 per cent gold will be considered. All of the alloys were made in an induction furnace. Each alloy was cast in a 3 by $\frac{1}{4}$ by $\frac{3}{4}$ -in. ingot. The method of obtaining the melting points and making color determinations was described in a previous paper.⁴ The Rockwell B scale with the $\frac{1}{16}$ -in. ball and 100-kg. weight was used for all hardness determinations.

The submersion of test pieces in concentrated nitric acid is one of the standard corrosion tests used in the optical trade. A test piece in the 50 per cent cold-worked condition, $\frac{1}{2}$ by 2 by 0.045 in., is blanked from a strip using a die, and the weight loss per square inch of surface is taken as a means of comparison. The time for this test is 2 $\frac{1}{2}$ hr. of actual submersion of the test piece in the acid. This standard test was applied to all of the 10-karat gold alloys discussed in this paper.

The tensile tests were made upon strips of the dimensions shown in Fig. 1. The test pieces after blanking were annealed at 1300° F. for 20 min. and cooled in air.

The "drop of the beam" method was used in determining the yield point, as there was a very marked "drop" when the yield point was reached.

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¹ References are at the end of the paper.

ALLOYS

Gold-copper-zinc Alloys.—In the gold-copper-zinc alloys the zinc replaced in part the copper content. The effect of this change on the physical properties is shown in Fig. 2. The hardness in the annealed condition is not affected greatly by this change in composition.

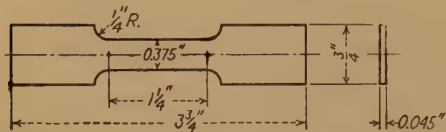


FIG. 1.—DIMENSIONS OF TEST STRIPS.

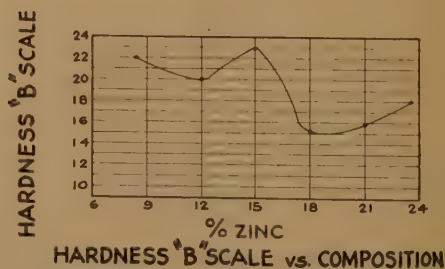
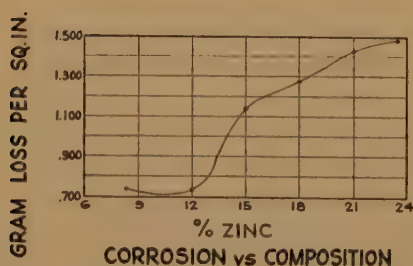
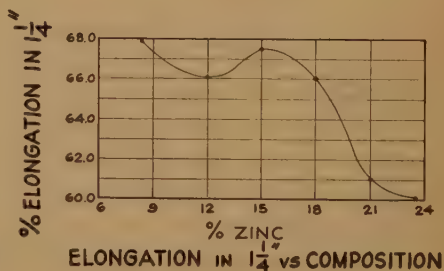
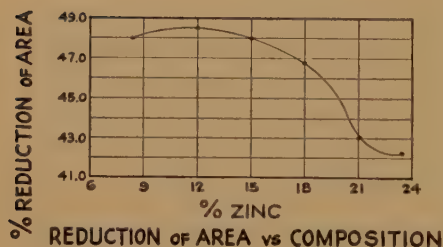
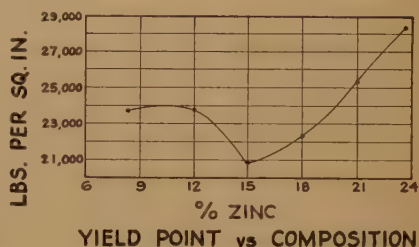
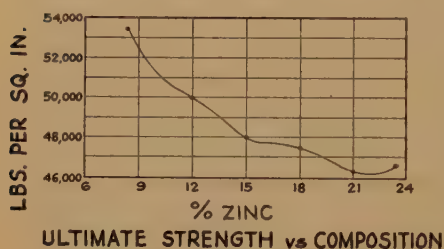
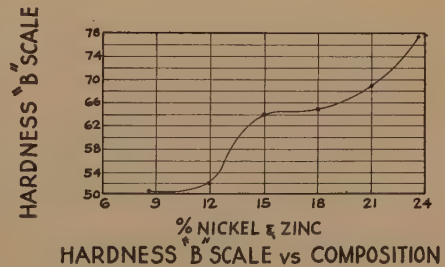
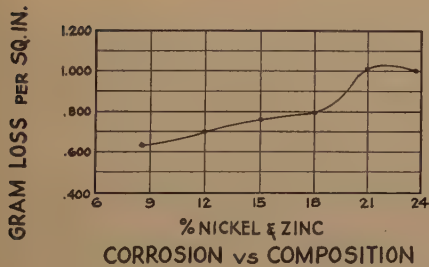
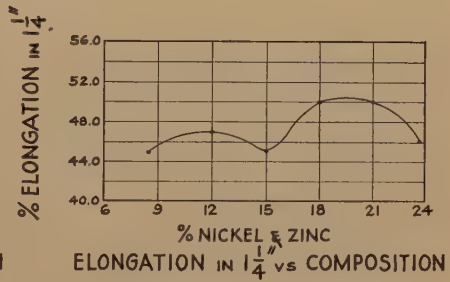
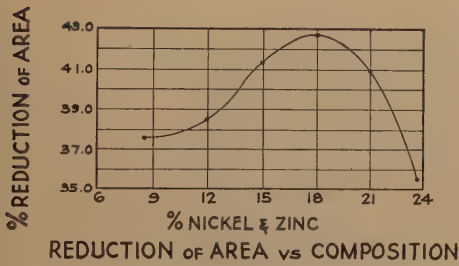
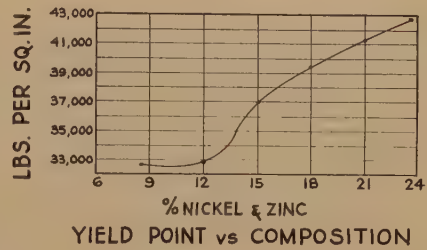
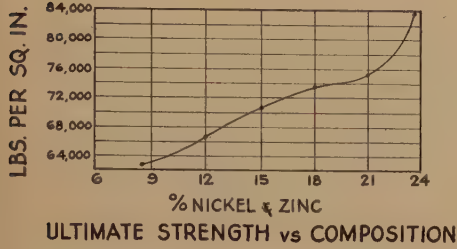


FIG. 2.—ALLOYS OF GOLD, COPPER AND ZINC.

The yield point increases slightly in the higher zinc alloys while the ultimate strength decreases, as the percentage of zinc increases. The elongation and reduction of area also decrease as the percentage of zinc

increases. The corrosion loss, as would be expected, increases rapidly with the increase of zinc.

These gold alloys are easy to melt and cast, and all fabricate readily. The low annealing temperature, melting point and corrosion loss limit the use of gold alloys of this type.



NICKEL AND ZINC-RATIO 1:1

FIG. 3.—ALLOYS OF GOLD, COPPER, NICKEL AND ZINC.

Gold-copper-zinc-nickel Alloys.—In this group (Fig. 3) zinc and nickel replace the copper in equal parts and a very pleasing group of white gold alloys is produced.

The hardness, yield point and ultimate strength increase as the percentage of zinc and nickel increase. The elongation and reduction of area increase with the increase of zinc and nickel up to about 18 per cent, then drop rapidly as the percentage of zinc and nickel continue to increase.

The melting point in this group of alloys remains fairly constant, while the corrosion loss increases as the proportion of zinc and nickel increases. The corrosion loss was not as great in this group of alloys as in the gold-copper-zinc group, the nickel having a tendency to retard the corrosion slightly when in combination with zinc.

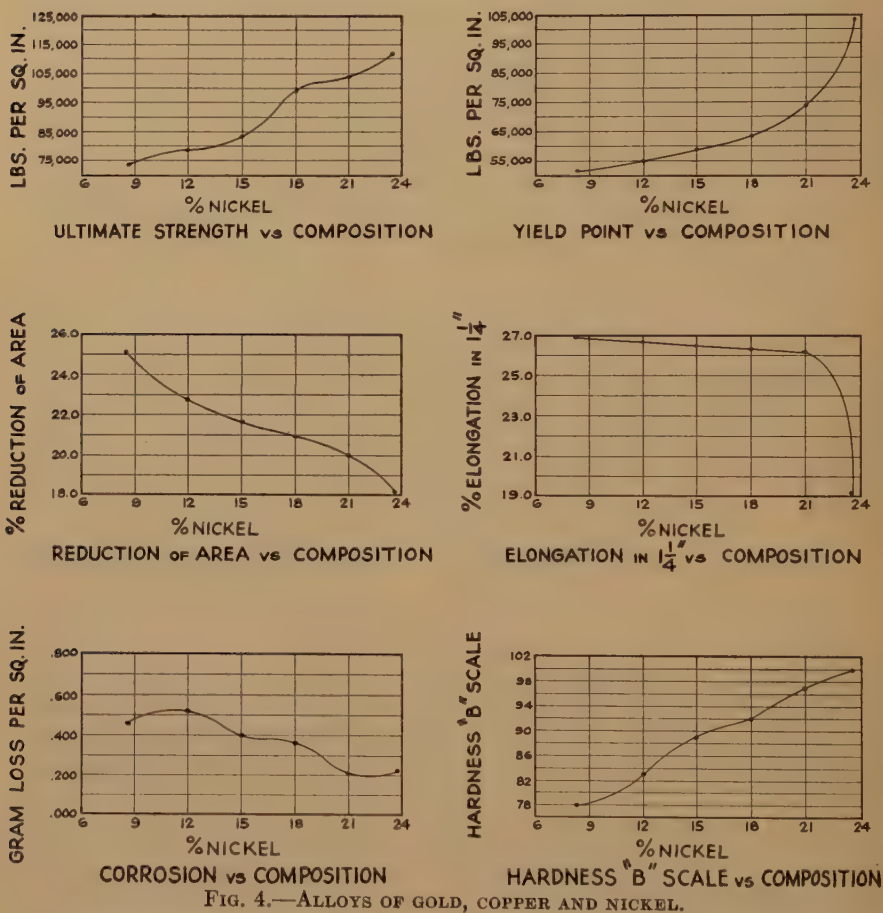


FIG. 4.—ALLOYS OF GOLD, COPPER AND NICKEL.

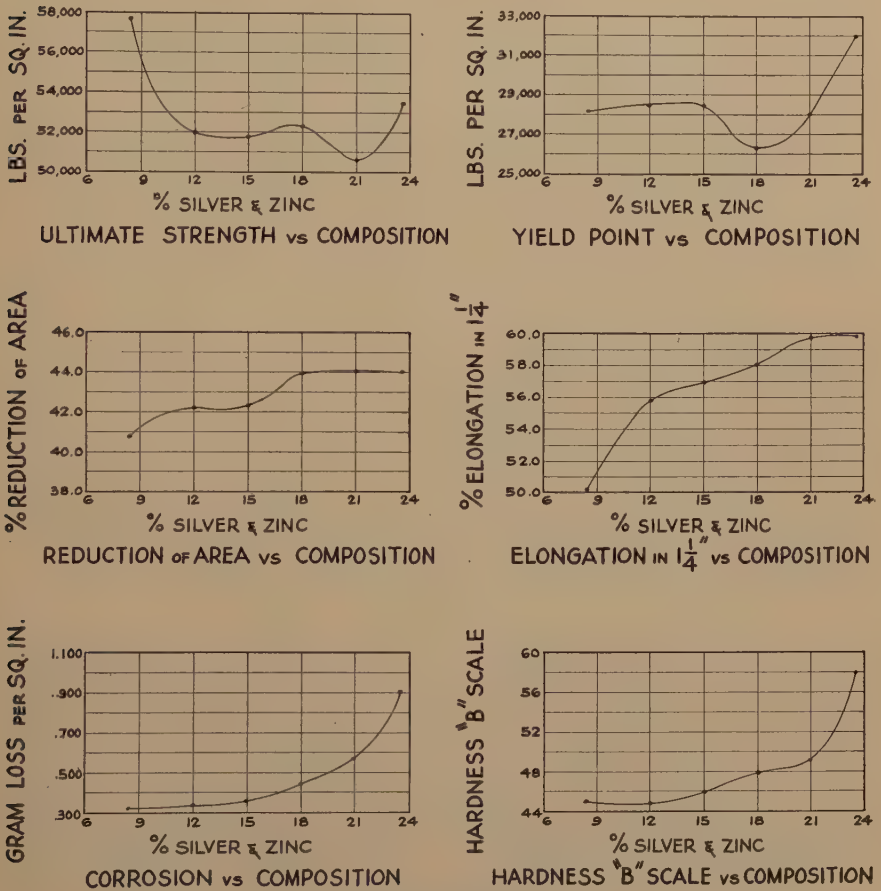
These alloys also are easy to melt and cast and fabricate easily and most of them can be used for commercial golds.

Gold-copper-nickel Alloys.—These alloys, (Fig. 4) using nickel to replace copper, are hard and possess high yield points and ultimate strengths. The hardness, yield point and ultimate strengths increase rapidly as the percentage of nickel increases. The elongation and reduction of area decrease as the nickel content increases.

The melting point being high, these alloys are difficult to cast and hard to fabricate. Heavy reductions must be used in rolling them, to

prevent fire-cracking. They will age-harden to some extent, although no great amount was observed.

The corrosion loss decreases as the percentage of nickel increases; just the opposite of the alloys in which zinc is present. The corrosion loss is far less when only nickel is used with the copper and gold than



SILVER AND ZINC-RATIO-1:1

FIG. 5.—ALLOYS OF GOLD, SILVER, COPPER AND ZINC.

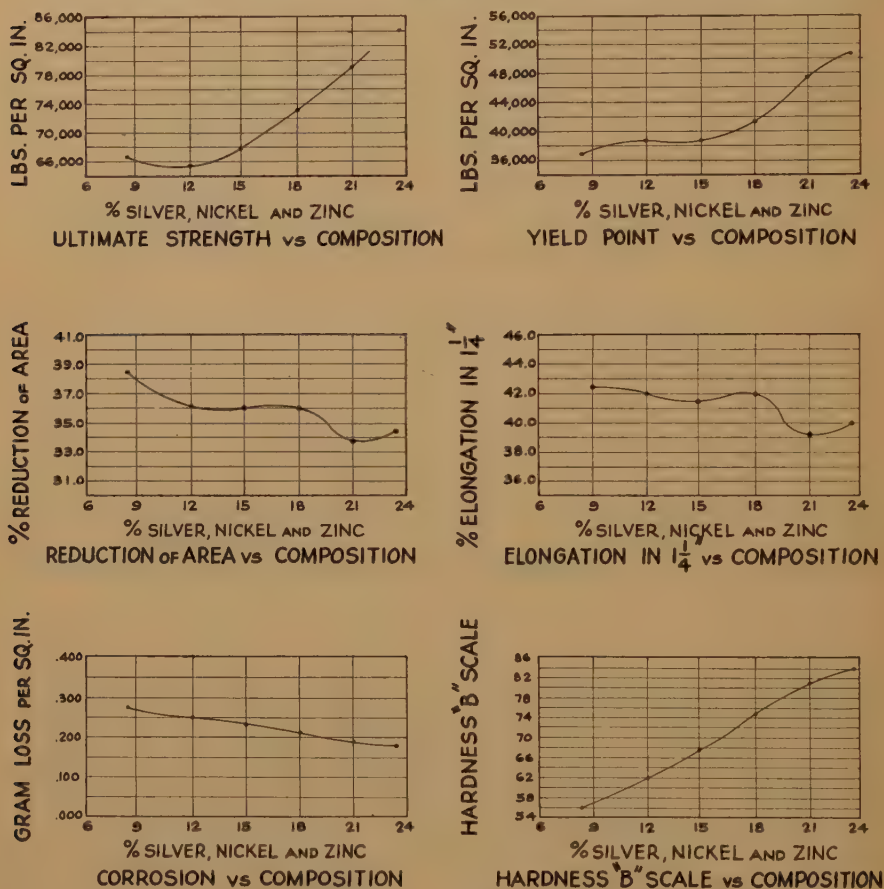
when zinc is present in the combination of zinc and nickel, or when zinc only is used.

The hardness and tensile strength will not permit all of these alloys to be used commercially.

Gold-silver-copper-zinc Alloys.—When silver and zinc are present in equal proportions instead of zinc alone, noticeable changes occur; for instance, see Fig. 5.

With the gold and copper in the same proportions as in the gold-copper-zinc alloys the hardness doubles, and as the percentage of zinc and silver increases the hardness also increases.

The yield point and ultimate strength increase in some alloys and in others decrease. The values obtained in the gold-silver-copper-zinc



SILVER, NICKEL AND ZINC-RATIO 1:1:1

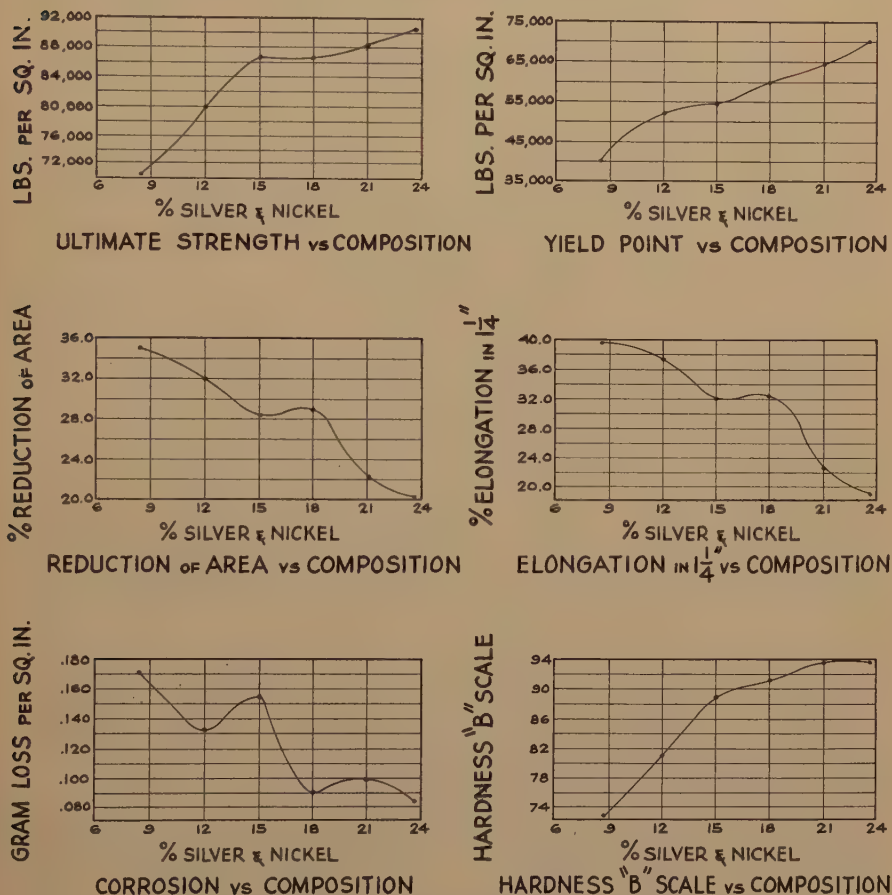
FIG. 6.—ALLOYS OF GOLD, COPPER, SILVER, NICKEL AND ZINC.

group were slightly higher for the same proportion of copper in the gold-copper-zinc alloys. The reduction of area and the elongation tend to increase as the amounts of zinc and silver increase—just the opposite of the alloy containing zinc but not silver.

The melting point and corrosion loss decreased as the percentages of zinc and silver increased. The corrosion loss was far less when silver and zinc were present together in the alloy than when zinc only was present.

Some of these gold alloys may be used commercially, as they have good physical and chemical properties.

Gold-silver-copper-zinc-nickel Alloys.—In this group of alloys, like the gold-copper-zinc-nickel group, the hardness, yield point and ultimate strength increase as the percentages of silver-zinc and nickel increase.



SILVER AND NICKEL - RATIO-1:1

FIG. 7.—ALLOYS OF GOLD, SILVER, COPPER AND NICKEL.

The hardness and yield point are slightly higher in these alloys than in the gold-copper-zinc-nickel series (Fig. 6).

The corrosion loss decreases as the silver, zinc and nickel content increases, opposed to the behavior of the gold-copper-nickel-zinc alloys.

These alloys may be used commercially if the color meets the requirements, as they alloy rather easily and present little difficulty during fabrication.

Gold-silver-copper-nickel Alloys.—When nickel and silver are present together, the hardness, yield point and ultimate strength are lower than when nickel only is present in the alloy (Fig. 7).

TABLE 1.—Data from Which Curves Were Derived

No.	Color	Composition of Alloy, Per Cent					Corrosion Loss, Grams per Sq. In.	Melting Point, Deg. F.	Yield Point, Lb. per Sq. In.	Ult. Str., Lb. per Sq. In.	Elongation, Per Cent in 1¼ In.	Reduction of Area, Per Cent	Hardness, Rockwell B Scale
		Gold	Silver	Copper	Zinc	Nickel							
GOLD-COPPER-ZINC SERIES													
3	Orange yellow	41.6		50.04	8.36		0.735	1720	23,800	53,400	68.0	48.0	22
6	Brass yellow	41.6		46.00	12.38		0.733	1700	23,800	50,000	66.0	48.6	20
9	Brass yellow	41.6		43.27	15.13		1.147	1670	20,800	48,000	67.6	48.0	23
12	Brass yellow	41.6		40.64	17.69		1.272	1640	22,300	47,400	65.0	46.8	15
15	Brass yellow	41.6		38.25	20.15		1.420	1610	25,300	46,200	61.0	43.0	16
18	Brass yellow	41.6		34.8	23.59		1.489	1570	28,400	46,600	60.0	42.2	18
GOLD-COPPER-ZINC-NICKEL SERIES													
2	Yellow-pink	41.6		49.8	4.12	4.44	0.627	1830	32,700	62,500	45.0	37.6	50
5	Light pink	41.6		47.0	5.60	5.79	0.698	1830	32,700	66,500	47.0	38.4	52
8	White-pink	41.6		43.8	7.23	7.35	0.767	1840	37,000	70,500	45.0	41.3	64
11	White-pink	41.6		40.83	8.58	8.93	0.778	1835	39,500	73,800	50.0	42.7	65
14	White	41.6		38.3	10.51	9.57	1.037	1825		75,000	50.0	41.0	69
17	White	41.6		35.33	11.04	12.03	1.000	1825	43,000	84,000	45.0	35.5	78
GOLD-COPPER-NICKEL SERIES													
1	Pink	41.6		49.64		8.76	0.468	1925	50,600	74,000	27.5	25.1	78
4	Blue-white	41.6		46.6		11.77	0.516	1960	55,000	79,400	26.7	22.8	83
7	Blue-white	41.6		43.54		14.83	0.400	1970	59,400	83,600			89
10	Blue-white	41.6		40.88		17.62	0.369	2005		99,500			92
13	Blue-white	41.6		38.05		20.36	0.209	2035	74,400	104,900	26.2	20.0	97
16	Blue-white	41.6		35.54		23.85	0.242	2045	104,100	111,200	19.0	18.0	100
GOLD-SILVER-COPPER-ZINC SERIES													
21	Pink	41.6	3.61	50.8	3.97		0.314	1720	28,200	57,700	50.0	40.8	45
24	Yellow	41.6	5.95	46.83	5.60		0.335	1680	28,500	52,000	56.0	42.2	45
27	Yellow	41.6	6.94	43.8	7.65		0.332	1640	28,200	51,800	57.0	42.2	46
30	Yellow	41.6	8.23	40.8	9.34		0.441	1610	26,200	52,400	58.0	44.0	48
33	Yellow	41.6	9.92	37.72	10.74		0.568	1580	28,000	50,600	60.0	44.0	49
36	Yellow	41.6	11.50	35.15	11.73		0.913	1550	32,000	53,500	60.0	44.0	58
GOLD-SILVER-COPPER-ZINC-NICKEL SERIES													
20	Pink	41.6	2.80	49.93	2.45	3.02	0.276	1775	37,200	66,700	42.5	38.3	56
23	Yellow-pink	41.6	3.85	47.01	4.02	3.5	0.254	1775	38,700	65,400	42.0	36.2	62
26	Yellow-pink	41.6	4.81	43.39	5.37	5.02	0.230	1745	38,700	67,900	41.6	36.0	68
29	Pale yellow	41.6	5.59	40.00	6.94	5.89	0.222	1720	41,700	73,100	42.00	36.0	75
32	Pale yellow	41.6	6.83	37.8	6.9	6.83	0.196	1705	47,600	79,200	39.2	33.7	81
35	White-yellow	41.6	7.7	34.9	8.1	7.7	0.184	1695	50,400	83,300	40.0	34.5	84
GOLD-SILVER-COPPER-NICKEL SERIES													
19	Pink	41.6	4.5	50.19		3.85	0.171	1805	40,000	70,000	40.0	35.2	72
22	Pink	41.6	5.37	47.24		5.78	0.132	1770	52,000	80,000	37.5	32.0	81
25	Pink	41.6	6.83	44.26		7.30	0.155	1795	54,100	86,800	32.0	28.2	89
28	Yellow-pink	41.6	8.29	40.76		9.34	0.090	1760	60,000	86,600	32.4	29.1	91
31	Light yellow	41.6	10.27	37.74		10.39	0.102	1775	64,400	88,200	22.6	22.0	94
34	White	41.6	11.11	34.9		12.14	0.085	1815	70,000	90,400	19.2	20.0	94

There is, however, an increase in the hardness, yield point and ultimate strength as the percentage of nickel and silver increases. The elongation and reduction of area decrease as the ultimate strength increases, and as the percentage of silver and nickel increases.

The melting point varies slightly with the increase of silver and nickel, while the corrosion loss in general decreases. The corrosion loss is less in these alloys than in the gold-copper-nickel group and less than in any of the alloys tested in this investigation.

It is possible to use these alloys, but they are hard to cast and do not fabricate easily.

GENERAL DISCUSSION

When silver is present in any of the 10-karat gold alloys, the corrosion loss is greatly reduced. Silver tends to change the brass yellow color to a milder and softer yellow shade.

Nickel is a whitening agent; it tends to reduce corrosion loss and increase the hardness, yield point and ultimate strength. Zinc, on the other hand, tends to increase the corrosion loss and decrease the hardness, yield point and ultimate strength.

All of the 10-karat gold alloys show a tendency to tarnish when submitted to a moist hydrogen sulphide gas test for 2 hr. All of the 10-karat gold alloys will stiffen to some extent upon aging, although the amount may be slight.

In this investigation it is difficult to say what causes the marked changes in the alloys of one particular group. At the time of writing this paper, the author is not in a position to say just what the exact causes may be, but it is suggested that intermetallic compounds play a very important part. It is almost impossible to compare one group directly with another group of a different composition, although the group may contain some of the same elements.

The data from which the curves were derived are shown in Table 1.

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Effect of Composition on Color and Melting Point of 10-karat, 12-karat and 14-karat Gold Alloys

By TRACY C. JARRETT,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1939)

THE alloying of various elements with gold to produce different colors is an old art, but the effect of each element or combination of elements is not generally known. Investigations have been made in this field by F. E. Carter,¹ E. M. Wise,² and L. Sterner-Rainer.³ It is the intent of this paper to present in schematic diagrams the effects of various elements upon the color and the melting point of gold alloys.

In this investigation 2-oz. melts made in a high-frequency induction furnace were used for all tests. The melting points were determined by the use of a calibrated chromel-alumel thermocouple sealed in a thin-walled alundum tube. The couple was then submerged in the molten metal and the freezing and melting points were determined by using a Leeds and Northrup potentiometer. By checking several melts using copper, zinc and gold, it was found that the accuracy of determining the melting point was within $\pm 5^\circ$ F.

To determine the differences in colors and to classify them, a wet tissue paper was placed over the polished samples and examined under a uniform white light. The 2 by $\frac{1}{2}$ by 0.045-in. samples were cut from 50 per cent cold-worked strip. The original ingot was 3 by $\frac{1}{4}$ by $\frac{3}{4}$ in. This visual comparison, although not scientifically exact, served as a quite satisfactory means for determining and classifying these differences.

The base alloys, or "hardeners," were first made up and analyzed, after which the gold and silver were added. This method of making up the alloys was chosen so that the same base alloy could be used for the gold alloys of different karats.

The first series consisted of gold, copper, zinc and nickel, the copper comprising from 85 to 65 per cent of the content of the "hardener" and the zinc and nickel replacing copper. The second series consisted of gold, silver, copper, zinc and nickel, the copper comprising from 85 to 65 per cent of the content of the hardener with the silver, nickel and zinc replacing copper.

There was no particular reason for choosing these combinations, except that they gave a color range from red-pink to white.

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¹ References are at the end of the paper.

ORANGE YELLOW		BRASS YELLOW
COMP % 41.6	GOLD	COMP % 41.6
50.04	COPPER	34.8
8.36	ZINC	23.6
1720°F	MELTING POINT ← INCREASE DECREASE →	1570°F

PINK		WHITE
41.6	GOLD	41.6
49.64	COPPER	34.55
8.76	NICKEL	23.85
1925°F	MELTING POINT ← DECREASE INCREASE →	2045°F

PINK		WHITE
41.6	GOLD	41.6
49.8	COPPER	35.33
4.44	NICKEL	12.04
4.16	ZINC	11.03
1830°F	MELTING POINT REMAINS CONSTANT	1830°F

FIG. 1.—10-KARAT GOLDS USING GOLD, COPPER, NICKEL AND ZINC.

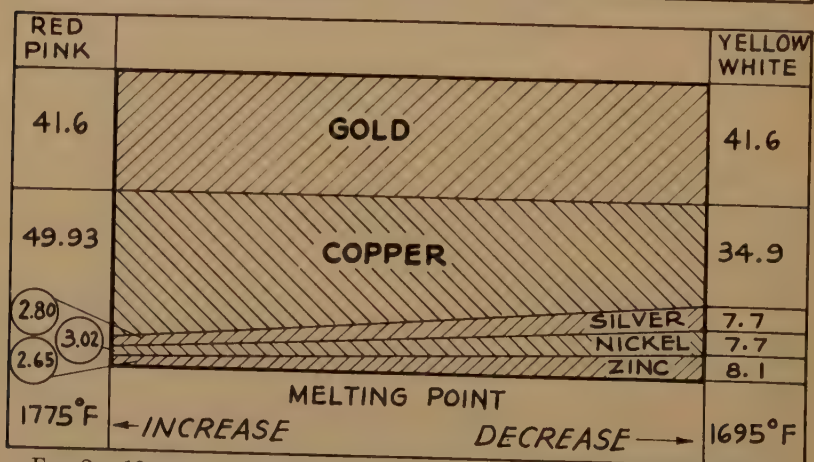
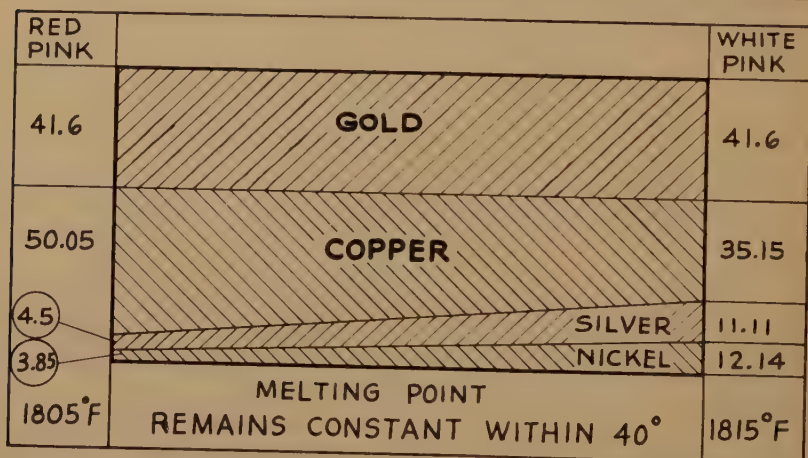
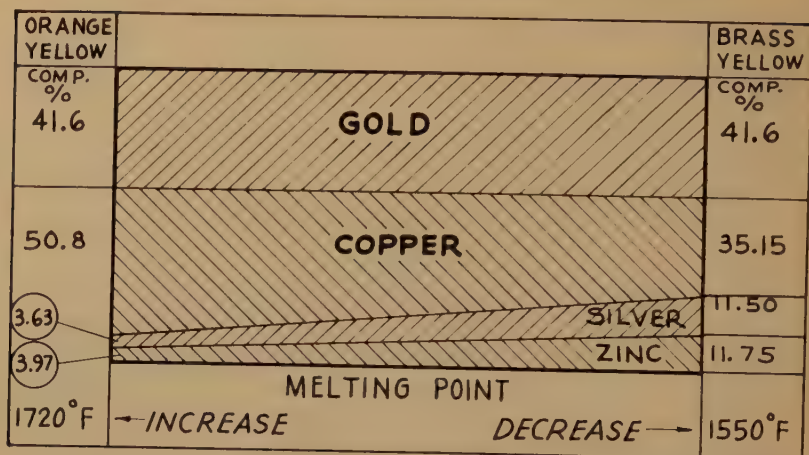


FIG. 2.—10-KARAT GOLDS USING GOLD, SILVER, COPPER, NICKEL AND ZINC.

ORANGE YELLOW		BRASS YELLOW
COMP. % 50.0	GOLD	COMP. % 50.0
42.85	COPPER	29.8
7.15	ZINC	20.2
1700°F	MELTING POINT ← INCREASE DECREASE →	1545°F

PINK		WHITE PINK
50.0	GOLD	50.0
42.5	COPPER	29.57
7.50	NICKEL	20.43
1865°F	MELTING POINT ← DECREASE INCREASE →	1980°F

PINK		WHITE
50.0	GOLD	50.0
42.67	COPPER	30.25
(3.8)	NICKEL	10.30
(3.53)	ZINC	9.45
1775°F	MELTING POINT REMAINS CONSTANT	1775°F

FIG. 3.—12-KARAT GOLDS USING GOLD, COPPER, NICKEL AND ZINC.

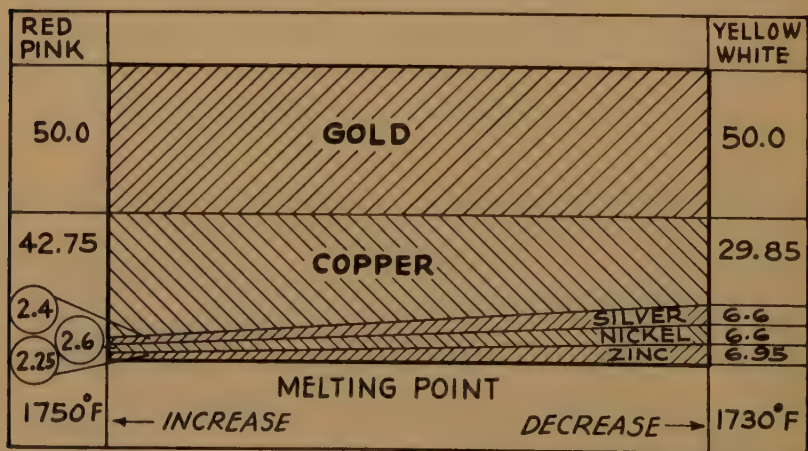
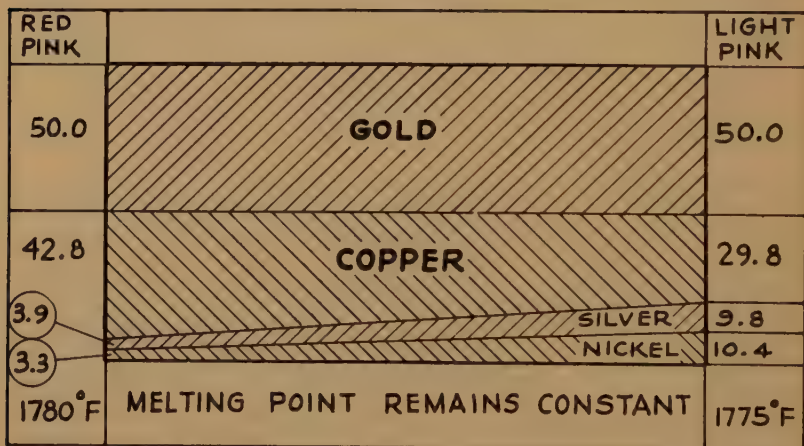
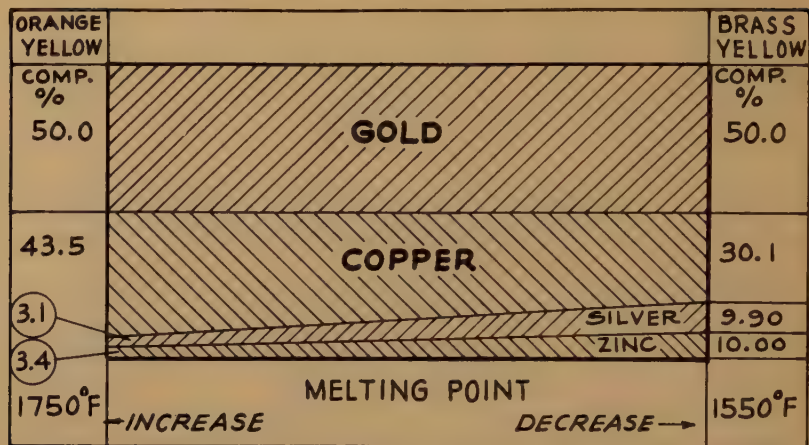


FIG. 4.—12-KARAT GOLDS USING GOLD, SILVER, COPPER, NICKEL AND ZINC.

ORANGE YELLOW		BRASS YELLOW
COMP. %		COMP. %
58.3	GOLD	58.3
35.74	COPPER	24.86
5.96	ZINC	16.84
1675°F	MELTING POINT ← INCREASE DECREASE →	1530°F

PINK		WHITE PINK
58.3	GOLD	58.3
35.45	COPPER	24.67
6.25	NICKEL	17.03
1820°F	MELTING POINT ← DECREASE INCREASE →	1920°F

PINK		WHITE
58.3	GOLD	58.3
35.59	COPPER	25.23
(3.17)	NICKEL	8.59
(2.94)	SILVER	7.88
1745°F	MELTING POINT REMAINS CONSTANT	1745°F

FIG. 5.—14-KARAT GOLDS USING GOLD, COPPER, NICKEL AND ZINC.

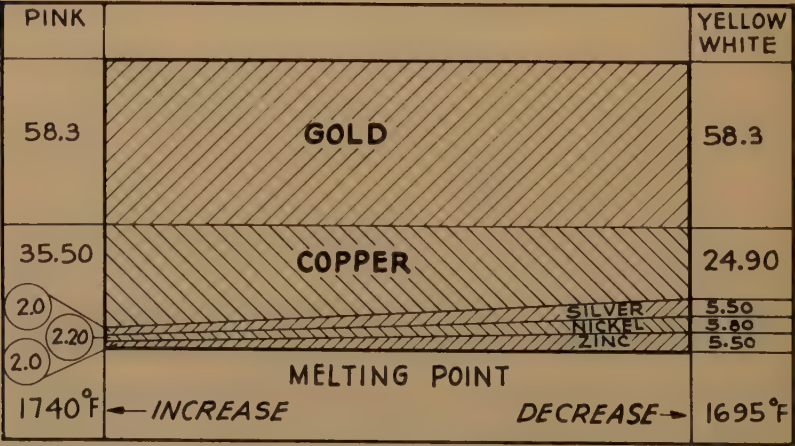
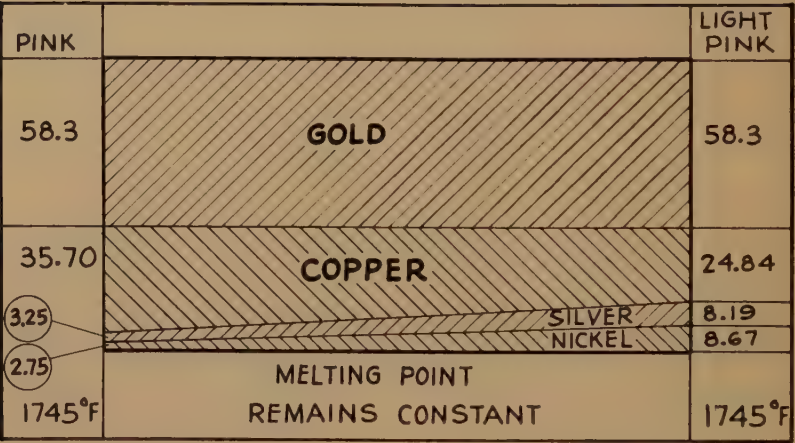
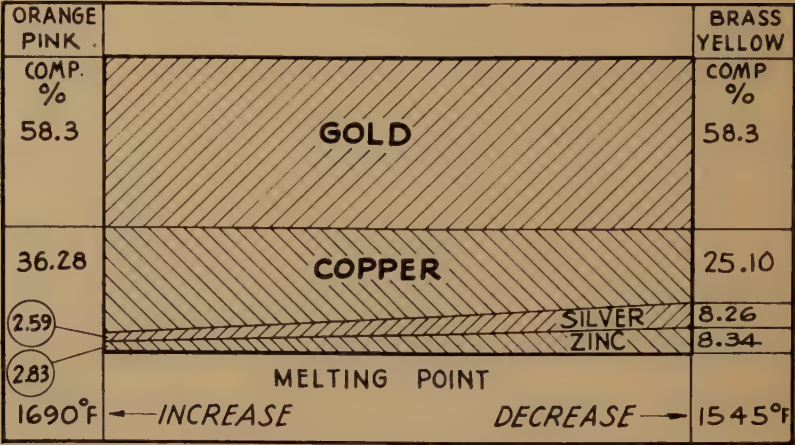


FIG. 6.—14-KARAT GOLDS USING GOLD, SILVER, COPPER, NICKEL AND ZINC.

In Figs. 1 to 6 the maximum and minimum composition limits are shown with their respective colors and melting points. The gold content, as shown in the diagrams, depending upon the quality, is kept constant, and the other elements are varied to produce the different colors.

10-karat Gold Alloys.—In the 10-karat gold alloys, it appears that with increasing amounts of zinc there is a decided change in the color from orange yellow to brass yellow (Figs. 1 and 2). When zinc and silver are added in equal amounts to the gold-copper alloy, the yellow color is still maintained. The melting points of the 10-karat gold alloys containing both zinc and silver are slightly lower than when zinc only is present, and in both cases the melting point is lowered as the zinc content is increased.

When increasing equal amounts of zinc and nickel are added to the gold-copper alloy, a trend toward white is apparent. With increasing (equal) amounts of zinc, silver and nickel, the color tends to go to the yellow-white side. The melting point, when zinc and nickel are present, remains constant, and when silver, zinc and nickel are present the melting point decreases as the proportions of these elements increase.

When nickel is added to gold and copper, the color becomes whiter as the nickel content increases, and the melting point increases. When nickel and silver in equal parts are added to the gold-copper alloy, the color tends to go to the white-pink as the nickel and silver content increases, while the melting point remains fairly constant.

12-karat Gold Alloys.—The principal differences between the 12-karat group (Figs. 3 and 4), and the companion group of 10-karat gold alloys are found in the nickel, copper, gold series. The white color produced by increasing the amount of nickel tends to go to the pink side in the 12-karat, while in the 10-karat it becomes whiter. The melting points of the 12-karat alloys as compared with the 10-karat in the same series are always slightly lower.

In the 12-karat group, using silver (Fig. 4), the melting points are sometimes slightly higher and sometimes slightly lower than corresponding 10-karat alloys. The color classification is practically the same.

14-karat Gold Alloys.—In the 14-karat gold alloys (Figs. 5 and 6), most of the melting points are slightly lower than those of corresponding 10-karat or 12-karat gold alloys. The colors are similar to the 10-karat and 12-karat series, but a few are slightly yellower or whiter.

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Effect of Cold-work upon Hardness and Recrystallizing Behavior of Pure Platinum

By E. M. WISE,* MEMBER, AND R. F. VINES,* JUNIOR MEMBER A.I.M.E.

(New York Meeting, February 1940)

It is known qualitatively that the recrystallization behavior of platinum is dependent upon the amount and particularly the nature of impurities present, the amount of prior cold-work and the annealing time and temperature, but published data are limited. A study of the effects of cold-work and annealing temperature on the hardness of a sample of very pure platinum was undertaken to supply part of this information.

CONCLUSIONS

1. The platinum used in the experiments had a probable platinum content of 99.99+ per cent, and had the following mechanical properties in the completely softened condition: Vickers hardness number, 39.4; ultimate tensile strength, 19,340 lb. per sq. in.; proportional limit, very low; elongation, 37.5 per cent in 2 inches.

2. The effect of cold-rolling on the hardness is shown in Fig. 1. The hardness increases rapidly up to 10 to 15 per cent reduction and more slowly up to about 75 per cent reduction, beyond which it increases more rapidly.

3. The recrystallization temperatures for a 15-min. anneal, after cold-rolling 19, 39.5, 50.8, 66, 80.5 and 89.5 per cent reduction in thickness, are approximately 765°, 700°, 635°, 600°, 545° and 425°C., respectively.

4. The recrystallized grain size of this platinum is a function of the percentage of cold reduction, being larger the lower the percentage of cold-work.

5. Little or no grain growth resulted from subjecting recrystallized samples to higher temperatures or annealing for longer times.

PRIOR WORK

As already mentioned, data on the recrystallization of platinum are scarce. Gmelin's¹ handbook, which summarizes data published earlier than August 1938, lists values ranging from 400° to 810°C. for the minimum temperature of recrystallization of samples with rather indefinite

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¹ References are at the end of the paper.

histories. The effect of annealing temperature on the tensile properties, hardness, electrical conductivity and grain size of cold-worked platinum has been studied by several investigators, but generally the observations have been limited to the effects obtained after a single degree of cold-work. Feussner² studied the recrystallization of *hot-worked* platinum and found the grain size to be larger the higher the annealing temperature and the lower the amount of hot-work. Wise and Eash³ determined the effect

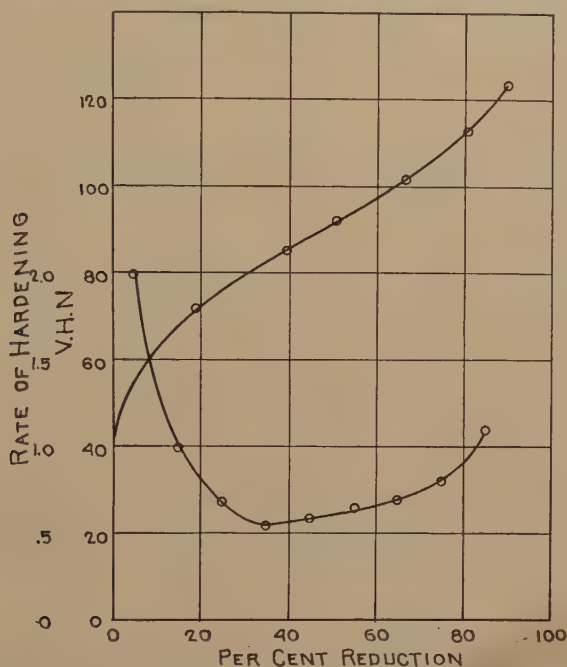


FIG. 1.—EFFECT OF COLD-ROLLING ON HARDNESS AND RATE OF HARDENING OF PLATINUM.

of annealing temperature on the tensile properties of platinum and platinum alloys reduced 50 per cent in area by cold drawing. They found that an annealing temperature of 1000° to 1100°C. was required to completely soften C.P. platinum in 5 minutes.

EXPERIMENTAL PROCEDURE

A 2 by 3½ by 0.240-in. thick bar of platinum that had been hard-rolled in a direction parallel to the 2-in. axis was employed. Samples from the same melt showed an electromotive force of plus 32 microvolts at 1200°C. against platinum of National Bureau of Standards Pt 27 purity, indicating a probable purity of 99.99+ per cent platinum. This bar had a Vickers hardness of 102 to 104 as received, which from the cold-rolling curve obtained later indicates that it had been cold-rolled about 72 per cent.

To provide wire for tensile tests, two pieces $\frac{3}{8}$ by 0.240 by $3\frac{5}{8}$ in. were cut from the bar and reduced to 0.092-in. wire by swaging with intermediate 15-min. anneals at 800°C. at approximate reductions of 50 per cent in area. A final cold reduction of 53.5 per cent in area was used in obtaining the 0.092-in. wire for test. The tensile tests were made in a 1000-lb. Amsler testing machine using either the 100 or 200-lb. scales. An Anderson extensometer with a 2-in. gauge length was employed. The proportional limit of the completely annealed samples was definitely below 2000 lb. per sq. in. but could not be determined accurately.

The remainder of the original bar was annealed at 800°C. for 15 min. and water-quenched. This treatment reduced the Vickers hardness number to 41.6. It was then cold-rolled to a reduction of 48.3 per cent, the direction of rolling being 90° to that used in the prior rolling. Reannealing as above yielded a Vickers number of 42.4. The bar was then re-rolled in the same direction to obtain a work-hardening curve. Pieces approximately $1\frac{1}{4}$ by 2 in. were cut from this bar after reductions in thickness of 19, 39.5, 50.8, 66, 80.5 and 89.5 per cent; the odd values being the result of a desire to avoid light passes and not more than two passes were employed between the reductions indicated. These pieces were cut into smaller samples and annealed at temperatures ranging from 300° to 1100°C.

A small electric furnace, automatically controlled, was used for the annealing treatments. The annealing times noted are times at temperature and unless otherwise mentioned the samples were water-quenched after annealing. Tensile-test wires were placed in small-bore refractory tubes for annealing to maintain straightness and were air-cooled after annealing.

Hardness tests were made on the Vickers hardness tester, using the diamond pyramidal indenter. Where possible, a load was selected to give a diagonal reading of 400 or more units, although loads less than 5 kg. or more than 30 kg. were not used. At least three readings were taken on each sample, the average being reported. In general the variation of the individual readings from the average value was less than one hardness number but on partially recrystallized samples greater variation was observed. On cold-rolled samples, the indentation diagonal parallel to the direction of rolling was longer than that in the direction perpendicular to rolling.

RESULTS AND DISCUSSION

Effect of Cold-rolling on Hardness.—Cold-rolling causes a rapid increase in hardness up to 10 to 15 per cent reduction in thickness, a more gradual increase between 15 and 75 per cent reduction and then a slightly more rapid increase up to 90 per cent reduction, as shown in Fig. 1. The latter increase is believed to be real and has been previously noted in the

tensile strength of cold-worked aluminum.⁴ Reductions above about 80 per cent also sharply alter the trend of the curve for recrystallizing temperature vs. percentage of reduction, as will be discussed later.

The rate of hardening (increase in hardness/percentage reduction), which was calculated for each 10 per cent interval, is shown in Fig. 1,

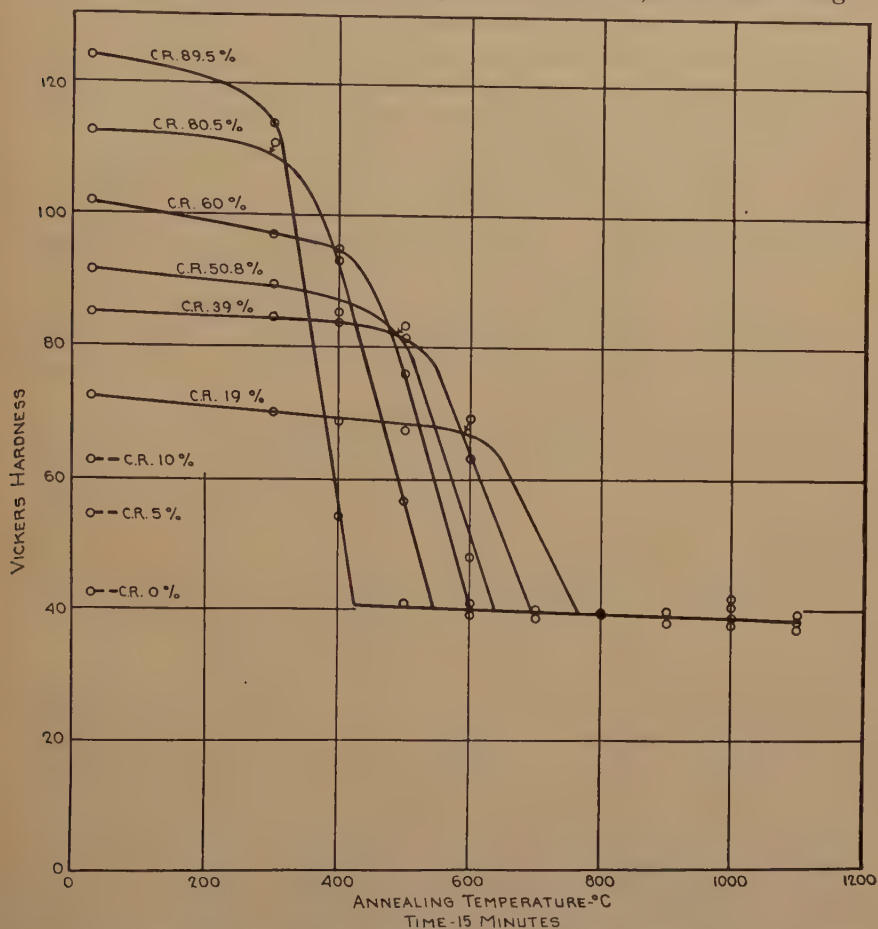


FIG. 2.—EFFECT OF ANNEALING TEMPERATURE ON HARDNESS OF COLD-ROLLED PLATINUM.

which indicates that the rate of hardening decreases rapidly up to 30 or 40 per cent reduction, gradually increases up to 70 or 80 per cent reduction and then increases rapidly.

Effect of Annealing on the Hardness of Cold-rolled Platinum.—Annealing curves for platinum, reduced 19 to 89.5 per cent in thickness by cold-rolling and annealed for 15 min. at temperatures ranging from 300° to 1100°C., are shown in Fig. 2. It is evident that as the percentage of cold reduction is increased, the minimum temperature necessary for complete

softening (complete recrystallization) is reduced. Observation of etched samples showed that completely softened samples had fully recrystallized. Once the sample has been completely recrystallized, the hardness is not materially lowered by increasing the temperature or (from the results of additional experiments) the time of annealing.

Effect of Cold-work and Annealing Temperature on Grain Size.—The pieces used in the annealing tests were etched without polishing to reveal the grain size near the surface. A number of etchants were investigated in an attempt to obtain a reagent that would selectively attack the grain boundaries, but none was found. Aqua regia, which was finally used, produces a rather flat etch, making grain counts rather difficult. In spite of this difficulty it was obvious from visual observation of etched samples that the grain size, once the sample had recrystallized, was not increased by higher temperature or longer anneals. It was also apparent that the ultimate recrystallized grain size was a function of the percentage of cold reduction, as generally occurs. These facts are not clearly brought out in Table 1, where the smallest amount of cold reduction was 19 per

TABLE 1.—*Relation between Amount of Cold-rolling and Grain Size Developed on Annealing*

Annealing Temperature, Deg. C.	Cold Reduction, Per Cent				
	19	39.5	50.8	66	80.5
	Number of Grains per Sq. Mm.				
1100	1.3	2.3	2.0	1.9	2.7
900	1.5	2.2	2.2	2.1	2.9
800	1.3				
700		1.8	2.2	2.0	2.2
600			2.1	2.1	2.2

cent, but they become increasingly evident at lower cold reductions. Thus, in samples cold-rolled 6.1, 8.1 and 10.2 per cent and annealed at 1100°C. for 15 min., the diameter of the average grain in the plane of rolling was approximately 5 mm., 2 mm. and 1 mm., respectively. A sample reduced 3.1 per cent did not recrystallize at 1100°C. but on annealing at 1316°C. recrystallized, yielding grains with an average diameter of 9 mm. in the plane of rolling. It should be noted that in these samples the maximum dimension of the grains was generally greater than the thickness of the sheet and it is possible that this may have had some influence upon the results. Torch annealing of the sample cold-rolled to 3.1 per cent reduction at a temperature near the melting point (1773°C.) did not increase the grain size beyond that obtained after annealing at 1316°C. Similarly, the grain size of a sample reduced

50.8 per cent was not noticeably larger after annealing at 1316°C. than after annealing at 800°C. Thus it appears that little if any grain growth occurs in this sample of platinum in the absence of stress. Other experimenters have noted that some samples of platinum behaved in a manner similar to that described herein, whereas other samples showed marked grain growth. Palladium also shows both behaviors. At present the factors responsible for these differences in behavior are not known.

Recrystallization Temperature.—From the hardness data, the recrystallization temperatures for platinum cold-worked 19, 39.5, 50.8, 66, 80.5

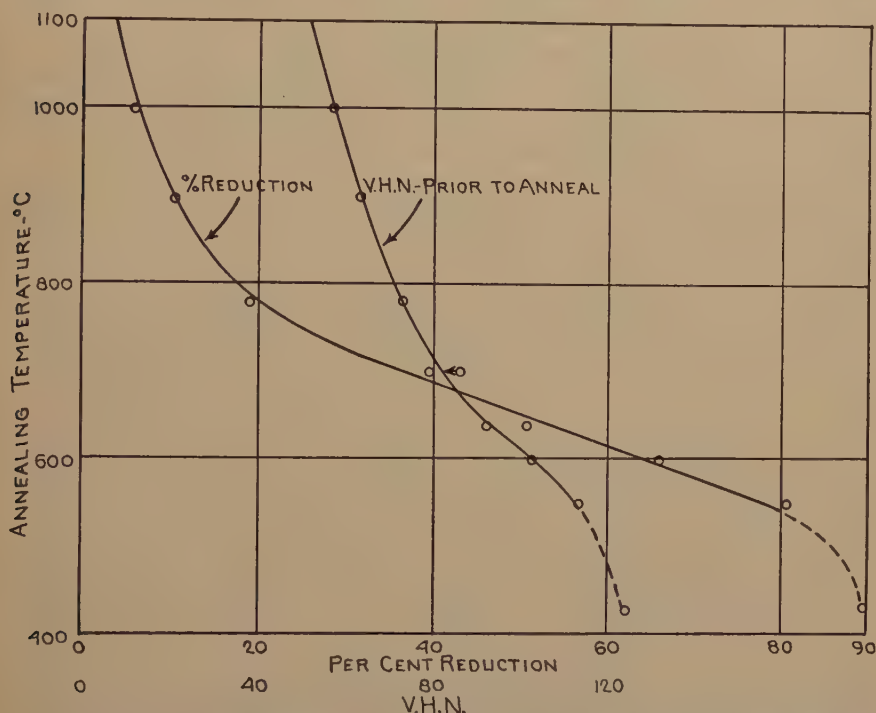


FIG. 3.—RELATION BETWEEN PERCENTAGE OF COLD REDUCTION OR COLD-ROLLED HARDNESS AND MINIMUM RECRYSTALLIZING TEMPERATURE OF PLATINUM FOR 15-MINUTE ANNEALS.

and 89.5 per cent reduction in thickness are approximately 765°, 700°, 635°, 600°, 545° and 425°C., respectively, for 15-min. annealings. Hardness changes become insensitive indicators of recrystallization at lower amounts of cold-work so visual observation of the changes in grain size was used in estimating the recrystallization temperatures for reductions below 19 per cent. The combined result of these hardness and grain-size studies is given in Fig. 3, which shows the approximate relation between cold-work and the temperature required to effect complete recrystallization in 15 min. Also included in this figure is the derived relation between the cold-worked hardness and the recrystallization temperature. From

this figure the marked effect of cold-work in decreasing the recrystallization temperature is apparent. The sample reduced 89.5 per cent in thickness appears to be out of line, but it is to be noted that this reduction is within the range where the rate of hardening upon cold-rolling increases rapidly. The minimum recrystallization temperature for a fixed reduction is also dependent upon the annealing time, but this was not extensively investigated. However, hardness numbers given in Table 2 show that platinum rolled 80 to 90 per cent can be completely recrystallized at 400°C. within 48 hours.

TABLE 2.—*Annealing-hardness Tests on Pure Platinum*
VICKER'S HARDNESS NUMBERS

Annealing time.....	As Rolled	Hours											
		¼	1	¼	1	48	96	¼	¼	¼	¼	¼	¼
Annealing temperature, deg. C.....		300	300	400	400	400	400	500	600	700	800	900	1000
Reduction, per cent:													
19.....	72.4	70	70.2	69.0	68.2	68.0	69.2	67.4	68.9	52.7	38.9	38.4	37.9
39.5.....	85.6	84.7	84.2	83.4	80.2	78.6	79.9	81.4	63.3	40.0	39.3	38.1	38.5
50.8.....	91.9	89.7	91.4	85.4	86.8	78.6	72.6	83.4	48.1	38.9	39.4	38.4	38.6
66.....	102	97.1	98.4	94.9	91.7	51.5	49.7	76.2	41.2	39.3	39.9	38.9	38.6
80.5.....	113	111	109	92.8	61.0	40.8		57.0	39.5	39.7	39.6	40.0	40.2
89.5.....	124	114		54.2	42.5	40.0	40.1	41.0	39.8	39.9	39.6	40.2	41.8

Tensile Properties.—The tensile properties of this platinum after cold-swaging to 53.5 per cent reduction in area to 0.092-in. dia. were: tensile strength, 29,500 lb. per sq. in.; proportional limit, 18,500 lb. per sq. in.; elongation, 4.5 per cent in 2 in.; hardness (on end of rod), 80.5 Vickers. It may be noted that the hardness values obtained on transverse sections of the swaged rods differed from hardness values obtained on sheet rolled to a similar reduction. The tensile-strength values of annealed samples of platinum were not as uniform as hardness values obtained on sheet. For samples annealed between 700° and 1100°C. for 15 min., the tensile strength averaged 19,340 lb. per sq. in., the minimum value being 18,350 and the maximum 19,900 lb. per sq. in. The change in tensile properties with annealing temperature over the range 700° to 1100°C. is scarcely greater than the scatter in the values for fixed temperatures, which is not surprising in view of the virtual absence of grain growth. The average tensile properties for this annealed platinum are: tensile strength, 19,340 lb. per sq. in.; proportional limit, very low; elongation, 37.5 per cent in 2 in.; hardness (on end of rod), 39.4 Vickers.

SUMMARY

The effect of cold-work and annealing temperature on the hardness, tensile properties, grain size and recrystallization temperature of a very

pure platinum has been determined. It has been shown that the recrystallized grain size, as disclosed by etching the unpolished surface, and the recrystallization temperature are complex functions of the percentage of cold reduction or the cold-rolled hardness. Time is also an important factor in determining the recrystallization temperature but has not been extensively investigated. Increasing the annealing temperature or time, once recrystallization has been completed, has very little effect on the grain size, hardness or tensile strength of this sample of platinum.

ACKNOWLEDGMENTS

The authors desire to thank Dr. F. E. Carter and Mr. C. S. Sivil, of Baker and Company, for the preparation of the high-purity, very soft platinum employed in this research, and Mr. A. J. Wadhams, Vice President of The International Nickel Co., for permission to publish this work.

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DISCUSSION

(Cyril Stanley Smith presiding)

G. SACHS,* Cleveland, Ohio.—It has been pointed out by Jeffries and Archer that abnormal grain-growth characteristics may be caused by the effect of the heating rate. Thus a very peculiar type of excessive grain growth causes some difficulties in copper manufacturing. The development of very large grains appears to be restricted to heavy reductions and low annealing temperatures, while higher annealing temperatures produce a medium-sized grain, probably because of the higher rate of heating.

C. S. SIVIL,† Newark, N. J.—Fig. 2 indicates that the Vickers hardness for annealed platinum is the same for all reductions; this is at variance with results we have obtained from tensile tests, which show that a lower reduction in area between anneals during working results in a metal of lower tensile strength and elongation than that obtained by heavy reductions. Using an 800°C. working anneal and a 15-min. final anneal at various temperatures, we have found a tensile strength of 18,900 lb. per sq. in. with a 26 per cent elongation in 2 in. for 50 per cent reductions between anneals, while for 93.8 per cent reductions the figures were 19,600 lb. per sq. in. and 35 per cent. The results were the same for all final annealing temperatures above that of full softening. If the working anneal was increased from 800° to 1200°C., we found only slight variations from these figures, with a tendency, however, to lower values.

As regards grain size obtained in the tests described above, we found that it was influenced by the temperature of final anneal—the higher the temperature, the larger the grain. The size was also affected by the temperature of the prior working anneal. However, the reduction between anneals had the greatest influence.

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† Physics Department, Baker and Co.

In explanation of the divergence of our results from those of the authors, we believe it lies in the difference of the size of test sample; we have used 0.050-in. wire and the grains were always smaller than the diameter of the wire, while Wise and Vines state that "the maximum dimensions of grains was usually greater than the thickness of the sheet."

We believe that other factors than temperature and reduction influence the recrystallization habit of platinum, and are investigating this phase of the problem. We mention this merely to advise caution in drawing conclusions at present on recrystallization phenomena in platinum.

B. BRENNER,* New York, N. Y.—In referring to relatively pure platinum, "commercial" (INCO) platinum is frequently better than plus 80 microvolts versus Pt 27 at 1200°C., or about 99.99 per cent pure. A differentiation, therefore, between "very pure" platinum of plus 32 microvolts versus Pt 27 at 1200°C. and "extremely pure" platinum, which might be zero to Pt 27, seems incongruous. However, aside from cold reduction and purity, the nature of impurity present certainly affects the recrystallization temperature. C.P. platinum wire minus 5 microvolts to minus 6 microvolts versus Pt 27 at 1200°C. with a corresponding purity (excluding gaseous impurities) of about 99.9999 per cent with a reduction of about 90 per cent recrystallizes at 400°C. within one hour. I consider elongation an excellent criterion for the progress of recrystallization.

In order to elucidate and understand the irregular behavior of C.P. platinum as to grain growth, it seems necessary to consider also the effect of absorbed oxygen that is liberated and migrates into the grain boundaries above about 600°C.

Some observations as to the effect of cold-work upon the tensile strength of C.P. platinum wire might be of interest here. With reductions of above 99.8 per cent, its tensile strength increases from 60,000 to over 100,000 lb. per sq. in. Wire thus reduced recrystallizes below 400°C. in about one hour.

F. E. CARTER,† Newark, N. J.—Before broad conclusions can be drawn on recrystallization of metals, several factors must be taken into account. Our experience with the recrystallization of platinum has made it clear that eventual grain size is very susceptible to previous work and heat-treatment.

W. B. PRICE,‡ Waterbury, Conn.—Not enough attention has been given to the effect of small impurities in inhibiting grain growth. Certain impurities in the third place of decimals will inhibit grain growth even though the alloy has been annealed five or six times at the same temperature. The grain size will remain the same when the material is annealed at higher temperatures.

H. E. STAUSS,§ Newark, N. J.—Several investigations on platinum in our laboratories have failed to produce concordant results. Some years ago a sample of sheet of slightly higher purity (as determined by thermal electromotive force) than that used by Wise and Vines was tested after 85 per cent cold reduction. A hardness curve similar to that of the authors was found, but with a sharper break between 300° and 400°C.; after annealing, the grain size, including any grain growth, decreased from 400° to 650°C., and then increased regularly to 1600°C. Later Mr. Sivil, also of our laboratories, tested another sample as wire and obtained results that tended to show that grain size was little affected by temperature. More recently tests on a much purer sample were made, again in wire form, and the grain size (including growth)

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† Physical Metallurgist, Baker Platinum Works.

‡ Chief Chemist and Metallurgist, Scovill Mfg. Co.

§ Research Physicist and Metallurgist, Baker and Co.

showed a definite maximum at an intermediate temperature, which is strongly reminiscent of a germinative temperature; but the maximum grain size decreased with either increased time of annealing or subsequent higher temperature annealing. We are investigating the causes of such contradictions at the present time.

If one may judge from platinum, some metals, perhaps only pure ones, are able to achieve a release of strains and a certain degree of atomic ordering and recrystallization before full, approximately perfect recrystallization takes place. The units in such cases, to judge from platinum, are larger and more rambling in appearance than those resulting from the later, more perfect ordering. The looser, less perfect structure apparently can organize a larger volume than the more perfect type of crystallization; and further annealing actually produces a diminution in grain size.

E. M. WISE AND R. F. VINES (authors' reply).—It is well known that several factors in addition to the amount of cold-work affect recrystallization behavior, but in our study the amount of cold-work was the important variable. Our conclusions, particularly those relating to freedom from grain growth, strictly apply only to platinum of similar purity processed as indicated. However, it is interesting to note that other investigators using platinum of equal or even higher purity obtained results on annealing temperature and tensile strength agreeing closely with those found by us.

With regard to Mr. Sivil's observations on the effect of the amount of prior cold-work upon the tensile strength of annealed platinum, it will be noted from Table 2 that there is also a tendency for the samples given high cold reductions to have a slightly higher annealed hardness than samples given low cold reductions. However, this difference is no greater than that produced by variations in annealing temperature for a single cold reduction, is almost within the limit of experimental error and would be difficult to show in Fig. 2. We also agree with Mr. Sivil with respect to the dominating influence of the amount of cold-work in determining grain size, but the increase in elongation with increased amounts of cold-work prior to the final anneal observed by him seems greater than would be expected from the change in grain size and may be due in part to the development of preferred orientation. In the event that minute inclusions of low solubility are present, their residual amount and size would be influenced by the prior annealing temperature.

Any divergence between our results and those of Mr. Sivil is probably not due to the size of the test sample, since most of our samples were thicker than the 0.050-in. diameter wire he used; the quotation "the maximum dimension of the grains was usually greater than the thickness of the sheet" applying only to specimens reduced 10.2 per cent or less.

The terminology employed in designating the purity of sensibly pure metals is inadequate and for this reason we stated the probable platinum content of the sample used, referring to it indiscriminately as "pure" and "very pure" in the text. As previously noted, the nature and state of combination of the impurities present are important in determining recrystallizing behavior but convenient and reliable methods of determining traces of impurities are not available.

R. F. MEHL, discussion on page 168.

Tensile Strengths at Elevated Temperatures of Fine Wires of Some Platinum Alloys

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(New York Meeting, February 1939)

THE short-time tensile-strength test, while it has not attained the practical importance of the creep test at elevated temperatures, has the advantage of being rapid and is satisfactory for determining relative strengths. For platinum and its alloys, which frequently are used at high temperatures under ill-defined conditions, the short-time test provides useful data that aid in the selection of the most promising alloy for each use. Measurements have been made upon 13 alloys, using wire 0.0031 in. in diameter, the choice of alloys and of wire size being determined by the requirements of a practical problem. Later the measurements were extended to higher temperatures by the use of heavier wire, 0.010 in. in diameter.

APPARATUS

The use of fine wire made the necessary equipment very simple, since no effort was made to measure the elongation. A small platinum-wound horizontal furnace was used, $\frac{1}{2}$ in. in internal diameter by 1 ft. long, with the wire threaded through it. The wire, clamped at one end while the other ran over a ball-bearing pulley, of a total length of 29 in., was loaded directly by running sea sand into an attached basket, making the rate of loading and not of elongation constant. The sand flowed from a funnel, under a head of 3 in., into the basket 3 in. below the orifice, at the rate of 170 grams per minute. Pulley friction and bending resistance of the wire as well as the force of impact of the sand could be neglected, being 3 grams and 0.5 grams, respectively. Furnace temperature was uniform within $\pm 5^\circ$ C. over a length of 3 in., although a drift with time occurred, the largest amount being 20° C. No provision was necessary for a controlled atmosphere.

In making the measurements, the furnace was brought to equilibrium before being used, and the temperature was measured with a platinum-platinum-10 per cent rhodium thermocouple and a high-resistance pyrometer before and after all the tests at one temperature. The wire sample, after being threaded through the furnace and attached to the

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basket, was drawn back into position, clamped, and immediately loaded to avoid elongation before the test proper. It was assumed that these fine wires reached temperature practically instantaneously. The test wire was always subject to an appreciable initial load, unlike the conditions of the standard tensile-strength test; this being constant and 35 grams, the weight of the basket, in the first series of measurements, and in the later series being made equal to 20 per cent of the breaking load as determined by a preliminary test.

RESULTS

The first tests, made on fine wires, were at moderate temperatures, but later, when it was decided to extend the temperature range, the fine wire was found too weak, and a larger size became necessary. Unfortunately, only a small supply was available and it was not possible to use this size at all temperatures, but it is obvious that different sizes, if loaded in the same times—that is, at the same rates per unit area—should yield identical results. Ransley and Smithells,¹ for example, have shown that with nickel the results of tensile-strength measurements with fine wires are in accord with those made on heavier wire. By test a loading rate of 980 grams per minute was found to be convenient and to give the same results as 170 grams per minute with the smaller size.

The measurements were made on two groups of alloys, all of approximately the same melting point and all solid solutions. One group, composed of binary alloys of platinum with rhodium or iridium and ternary alloys with rhodium and iridium, was received as wire at 0.010 in., after somewhat varied histories. These were annealed at 1200° C. and drawn to 0.0031 in., a reduction of 90 per cent. The other group, composed of ternary alloys of platinum with rhodium and ruthenium, received a reduction of 98.5 per cent from 0.025 in. to 0.0031 in., after an anneal at 1000° C. The alloys were tested in both the hard and the annealed condition. Although above the annealing point the measurements on the hard wire should be the same as for annealed metal, all the data are given to show the manner of the change of strength as the annealing temperature range is crossed. This information is helpful in understanding similar behavior in annealed wire, if the heat-treatment has not fully removed the working strains.

The two sets of wires were tested independently, and each set was tested separately in the hard and annealed condition. The alloys were tested in random order at each temperature to avoid spurious results from any furnace drift and the temperatures were selected in irregular order to reduce systematic errors that might arise as the measurements progressed. Three trials were made with each alloy at every temperature and the averages are given in the figures, in smooth curves.

¹ References are at the end of the paper.

In this experiment the important data are the relative behaviors, as represented by the smooth curves, of a number of alloys, and the general behavior of all the alloys as the temperature of testing is increased. The numerical values of the tensile strengths at each temperature, being subject to a number of chance errors and being determined in a special manner, are less important, and may even be misleading if compared with other experiments. For these reasons the results are given simply in grams breaking load; although, for completeness, the tensile strengths are

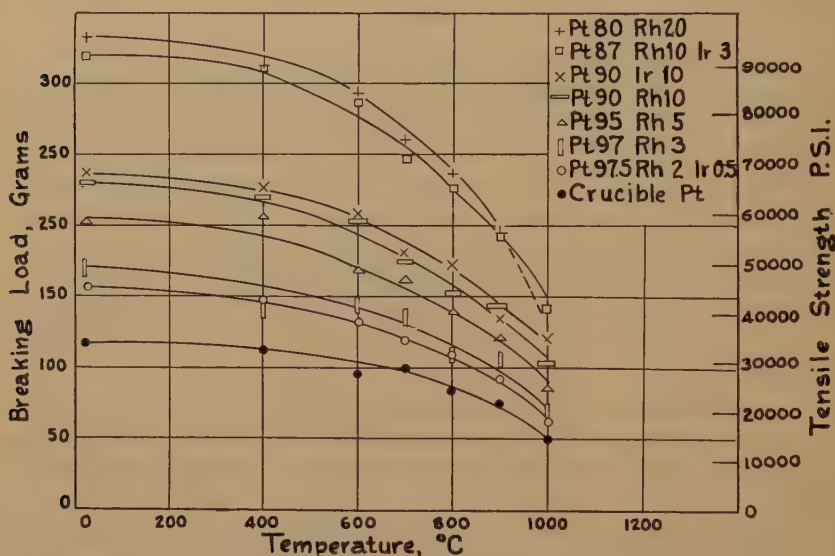


FIG. 1.—BREAKING LOADS OF FIRST GROUP OF WIRES WHEN HARD-DRAWN 90 PER CENT.

indicated in the figures. The conversion factor to change from breaking load to tensile strength in pounds per square inch is 292.

DISCUSSION OF RESULTS

The alloys almost invariably maintained their relative strengths at all temperatures, either when hard, as in Figs. 1 and 2, or annealed, as in Figs. 3 and 4. Wise and Eash² found a similar result with platinum alloys and palladium alloys separately at temperatures up to 1100° C., except that platinum with 10 per cent rhodium maintained its strength better than the other alloys. The present results do not show any essential differences between rhodium and iridium alloys. Ransley and Smithells,¹ in testing different grades of nickel, found that, except for a special refined nickel, all maintained their relative strengths to 1000° C. Thus it appears to be true that solid solutions of the same predominant metal maintain their relative order of strengths at all temperatures not too close to the melting point.

Comparison of the curves for annealed and hard-worked wires, particularly Fig. 3, show that the fully annealed alloys tend toward a linear relation between decline in strength and increase in temperature, although there is still a change in the relation at the annealing point. Wise and Eash² found much the same linear relation, using temperatures to 1100° C., although Ransley and Smithells¹ found it only in a specially refined nickel and observed arrests at 300° to 450° C. with the other grades. Hard wires exhibit a marked drop in strength at the annealing

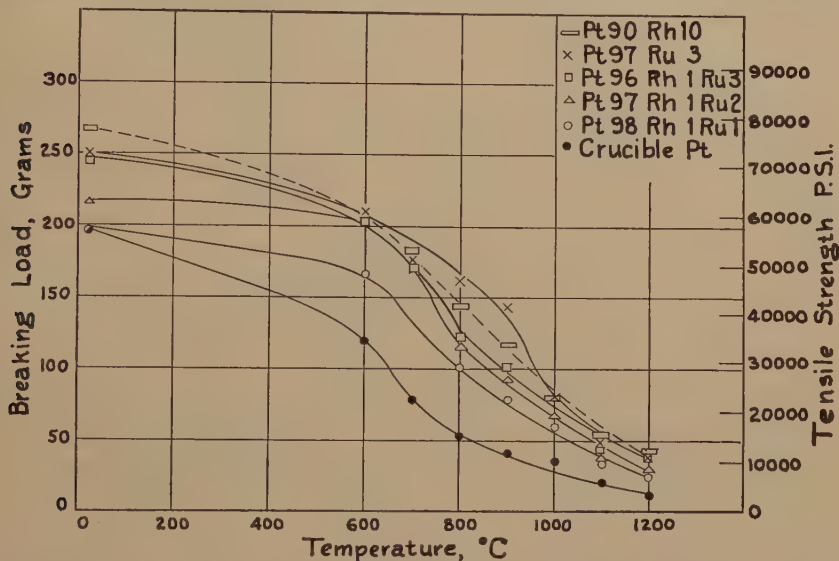


FIG. 2.—BREAKING LOADS OF SECOND GROUP OF WIRES WHEN HARD-DRAWN 98.5 PER CENT.

point, and the question arises whether similar breaks in the curves of annealed wire indicate incomplete removal of initial internal working strains or merely a difference in the rate of removal, above and below the annealing range, of the strains developing during the test itself.

In Fig. 3 the curves extrapolate naturally to the solidus points, showing how the melting points will modify the relative order of strengths at temperatures sufficiently high to make the differences in melting point significant. A corollary of an approximately linear temperature-tensile strength curve is that the melting point has a profound influence upon the short-time tensile strength. At a temperature that is a given fraction of the melting point, a metal maintains the same fraction of its tensile strength, which in the centigrade system should be measured at 0°. Thus, of two alloys of equal strength at room temperature, at an elevated temperature the stronger one will be that with the higher melting point. Or, all alloys showing such a linear relation, at temperatures that are equal fractions of their respective melting points, retain equal fractions

of their strength as measured at the base temperature. Thus the alloys of Fig. 3 maintained 46 to 47 per cent of their strengths at half their melting points. The data of Wise and Eash² show that platinum at half its melting point ($887^{\circ}\text{C}.$) retained 32 per cent of its strength, and palladium

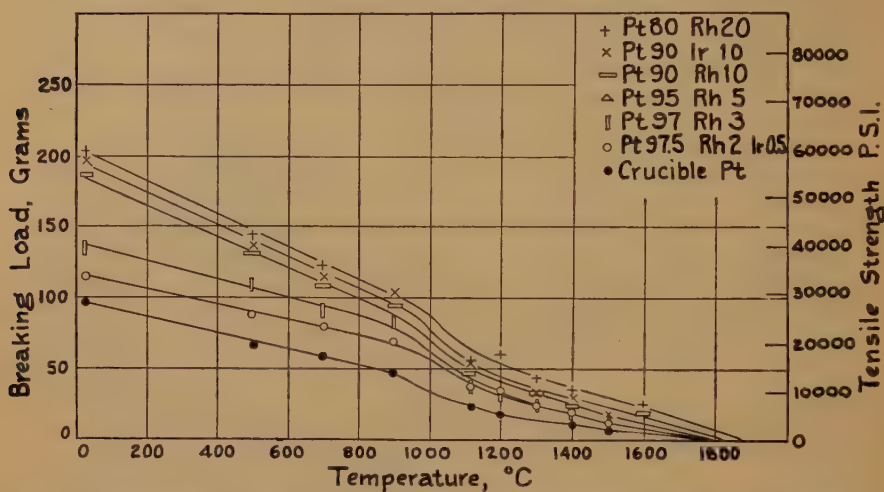


FIG. 3.—BREAKING LOADS OF FIRST GROUP OF WIRES WHEN ANNEALED AT $1200^{\circ}\text{C}.$

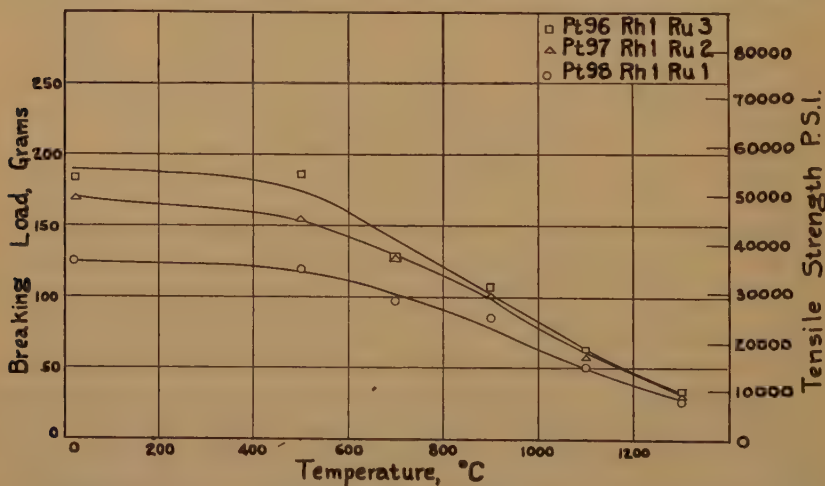


FIG. 4.—BREAKING LOADS OF SECOND GROUP OF WIRES WHEN ANNEALED AT $1200^{\circ}\text{C}.$

($777^{\circ}\text{C}.$) retained 34 per cent, while Ransley and Smithells,¹ also deforming their samples at a constant rate, found that a refined nickel ($726^{\circ}\text{C}.$) retained 31 per cent of its strength in close agreement with the results of Wise and Eash. The difference from the present results may lie in the different manner of testing. On the other hand, Wise and Eash² found that at $1100^{\circ}\text{C}.$, platinum, with a melting point of $1773^{\circ}\text{C}.$, retained

16.6 to 18.8 per cent of its strength, while palladium, melting point 1554° C., retained only 10 to 11.2 per cent.

CONCLUSIONS

1. Alloys that are simple solid solutions with practically equal melting points maintain their relative order of strengths at all temperatures not too close to the melting point.

2. The loss in strength with increase in temperature tends to be an approximately linear relation in a fully annealed solid solution. Material with working strains shows a rapid decrease in strength at the annealing range of temperatures.

3. As a result of the linear relation, it follows that different alloys retain equal fractions of their strengths at equal fractions of their melting points and that a higher melting metal maintains its strength better than a lower melting one.

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2. Wise and Eash: *Trans. A.I.M.E.* (1938) **128**, 282.

DISCUSSION

(*Frances Hurd Clark presiding*)

R. VINES,* Bayonne, N. J.—The conclusions drawn by Dr. Stauss would be particularly useful if they could be used to estimate strengths at high temperatures from known room-temperature properties. However, it appears that conclusions 1 and 3 are contradictory. Conclusion 1 (that the alloys maintain their relative order of strengths at all temperatures) is apparently valid for the alloys that were tested, but certainly would not be if platinum alloys melting at a lower temperature than pure platinum had been included in the tests. For example, a 20 per cent Ni, 80 per cent Pt alloy would have a tensile strength, at room temperature and in the annealed condition, higher than any of the alloys used by the author, but at 1500°C. it would be partly molten. However, conclusion 3 (that the higher melting alloy maintains its strength better than a lower melting alloy) would apply in either case. This conclusion is also in agreement with the results given by Wise and Eash, who showed that a 10 per cent rhodium-platinum alloy, the highest melting alloy they used, maintained its strength better than the others.

The author used an extremely rapid rate of loading for such fine wires, and the time of loading for the weaker wires was as low as 6 sec. A finite time would be required to note that a wire had broken and shut off the sand. I believe this overshooting of the breaking load is at least partly responsible for the fact that the author found that platinum maintained 46 to 47 per cent of its strength at half the melting point in contrast to the 31 per cent found by Wise and Eash.

The author said that he did not think this was so, as the curves extrapolated naturally to the melting point. I replotted the reported values on a more open scale and found that the points, especially those from 1100° to 1500°C., did not lie on a smooth curve and that the curves drawn could be extrapolated with equal accuracy to various temperatures, depending upon how the drop at 1000°C. (Fig. 3) was

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weighted. Since there are no values reported for 1000°C. and the test procedure was changed between 900° and 1100°C., the data available do not permit extrapolation.

H. E. STAUSS (author's reply).—Conclusions 1 and 2 are supplementary, not contradictory; or perhaps somewhat more logically, conclusion 1 is a specialized corollary of conclusion 3. Conclusion 1 applies under certain limited conditions, and under these conditions indicates that curves of the type shown in the figures of the text do not cross before the final intersections as they approach their respective melting points (solidus points, of course). The example of the platinum-nickel alloy somewhat stretches the important qualification in the paper of "practically equal melting points," and obviously its curve would have to cross the others at a lower temperature than did the alloys under test. Conclusion 3 is the more general formulation, but is in the nature of an extrapolation of the experimental results given in the paper.

The error suggested by Vines is the overshooting of the breaking load because of the time required to intercept the sand stream. Essentially this is the reaction time of the operator. This error produces a displacement of the breaking load-temperature curves parallel to themselves, but does not change the slope. However, this error will cause increasing fractional errors in the breaking loads as the latter decrease. The magnitude of the overshooting is not great enough to account for the difference observed (31 per cent for Wise and Eash and 45 to 47 per cent for me) of the original breaking load at half the melting temperature. The 6 sec. is the shortest time, not a constant time. The values 45 to 47 per cent given in my paper do not depend upon single determinations upon platinum but upon many measurements on many alloys with greatly different breaking loads and times of breaking, an indication that there is no large systematic error. The curves can be extrapolated as a group, without forcing, to their respective solidus points, and there seems to be no reason for extrapolating them elsewhere or for assuming a large systematic error.

The difference in the fraction of strength maintained at high temperatures as determined by various investigators lies rather in the differences in experimental procedures. The earlier workers used a constant rate of straining or stretching; I used a constant rate of stressing or loading. Neither is completely right; both were convenient. In both cases the wires finally broke from the integrated results of complex time-load relationships. If the constant rate of loading produces the more nearly linear relation between breaking load or tensile strength and temperature, this is an important point in its favor. It is not, however, the purpose of the paper to insist that such is the case.

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